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THORIATED TUNGSTEN FILAMENTS.

BY

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SUMMARY.

The rate of evaporation of electrons, ν_e, from a thoriated tungsten filament depends on the temperature T and on θ, the fraction of the surface covered by thorium atoms. The relation of ν_e to θ and T has been given by Brattain and Becker. From ν_e the change in contact potential V of the filament surface produced by the adsorbed thorium can be calculated by the Boltzmann equation. Knowing σ the number of thorium atoms per cm.^{2}, the dipole moment M of each is given by $V = 2\pi\sigma M$. By an equation already used for Cs films on tungsten, the 2-dimensional equation of state of the adsorbed film can be calculated from M. Then by Gibbs' adsorption equation the relation of the atom evaporation rate ν_a to θ and T can be determined. It is thus calculated that in the range from $\theta = 0.2$ to $\theta = 0.6$, ν_a varies in proportion to $\epsilon^{H\theta}$ where $H = 8.1$ in good agreement with the value $H = 7.8$ given by Brattain and Becker's measurements. A recalculation of the data of numerous experiments in 1921–1923, using the new relations of ν_e to θ, gives data on ν_a as a function of T and θ in good agreement with the values of ν_a calculated from ν_e.

The diffusion coefficients of Th through tungsten crystals, along grain boundaries and over the free filament surface, are calculated. A theory is given for the cause of the variation in the surface diffusion coefficient with σ. The probable mechanism of the production of the metallic thorium within the filament is discussed. At 2400° the thorium which arrives at the surface along grain boundaries, for some unknown reason, does not spread out over the surface as it does at lower temperatures (1900–2100°).

A study of the electron emission of tungsten filaments containing approximately one per cent. of ThO_2 [1] showed that after proper heat treatment of the filament the electron emission at 1500° K. was about 100,000 times greater than

[1] I. Langmuir, *Phys. Rev.*, **22**, 357 (1923).

that from pure tungsten. To bring the filament into this condition it is first heated for a few minutes to a temperature above 2800° K. This generates in the filament a low concentration of metallic thorium in solid solution. The filament is then heated for a considerable time to an activating temperature between 1800° and 2200° which allows some of the metallic thorium to diffuse to the surface of the filament where it forms a monatomic adsorbed film. Even prolonged activation does not cause the film to become more than 1 atom in thickness. To determine the extent to which thorium has accumulated on the surface of the filament, the "activity" is found by measuring the saturation electron emission at a "testing" temperature chosen so low that diffusion of the thorium from the interior does not take place and that the thorium content of the surface film does not change by evaporation. Temperatures from 1250° to 1600° are most convenient testing temperatures.

If the filament is heated to temperatures above about 2200°, thorium atoms evaporate from the surface sufficiently rapidly to "deactivate" the filament. The progress of this deactivation can be followed by interrupting the deactivation from time to time to test the activity by measuring the emission at the standard testing temperature.

Study of activation curves furnishes knowledge of the rate of diffusion to the surface, whereas deactivation curves give data for determining the rate of evaporation of thorium as dependent on the temperature and on the amount of thorium on the surface.

To make these studies quantitative it is necessary to have a measure of the number of atoms in thorium present at any time in the adsorbed film. In 1923 this was done by assuming that each adsorbed thorium atom on the surface constitutes a dipole of moment M which results from the positive charge of the adsorbed thorium atom; the evidence for such a charge consists in the fact that the presence of a complete adsorbed film of thorium raises the contact potential by about 1.4 volts. If it be assumed that the dipole moment of each thorium atom is independent of the presence of its neighbors, the contact potential must vary linearly with σ, the number of adsorbed thorium atoms per unit area. From the Boltzmann

equation it then follows that the logarithm of the electron emission at a given temperature should vary linearly with σ.

From the nature of the forces holding adsorbed atoms in the surface film it was concluded that the maximum number σ_1 of adatoms [2] which can be packed into a monatomic film is definitely related to the number of atoms in the surface lattice of the underlying metal. The number of tungsten atoms per square centimeter is 1.425×10^{15} atoms per sq. cm. Since the thorium atoms are much larger than the tungsten atoms, they could not be as tightly packed as the tungsten atoms. It is therefore assumed that the complete thoriated film contains one thorium atom for every two tungsten atoms, giving

$$\sigma_1 = 7.12 \times 10^{14} \text{ atoms cm.}^{-2}. \quad (1)$$

The condition of the adsorbed film can thus be conveniently described in terms of the covering fraction θ which may be defined by

$$\theta = \sigma/\sigma_1. \quad (2)$$

From these considerations it follows that the logarithm of the electron emission at a given temperature varies linearly with θ, and therefore if we represent by θ' the value of θ calculated in this way by assuming M to be constant, we have

$$\theta' = [\log (i/i_0)]/[\log (i_1/i_0)], \quad (3)$$

where i_1 is the maximum electron emission corresponding to complete activation and i_0 is the electron emission from pure tungsten at the same temperature.

Experimentally it was found in activation curves that $\log i$ increased approximately linearly with time, whereas the curve giving i as a function of time had a high upward curvature. This was interpreted as indicating that the rate of arrival μ in atoms cm.$^{-2}$ sec.$^{-1}$ of the thorium at the surface was approximately constant during the activation curve, and seemed to lend support to the linearity of the relation between θ and the logarithm of i. However, when θ' was plotted against the time, t, it was found that θ' increased at first

[2] J. A. Becker, *Trans. Amer. Electrochem. Soc.*, **55**, 153 (1929), has suggested this term for adsorbed atoms.

approximately linearly but the rate of increase then gradually decreased until it approached zero as θ approached unity. Activation curves at temperatures from 1950° to 2050° which gave maximum activities corresponding to $\theta' = 1$, showed that with a relatively high degree of accuracy,

$$d\theta'/dt = k(1 - \theta'). \tag{4}$$

To account for the presence of the factor $(1 - \theta')$ the hypothesis was made that the thorium atoms which arrived from the interior pushed the adatoms off the surface if they arrived at a place already occupied. This forced evaporation was referred to as "induced evaporation" to distinguish it from that which occurs spontaneously at a given temperature from the film, even when thorium does not arrive from the interior.

From a study of activation and deactivation curves, and by means of the foregoing theory, the diffusion coefficient of thorium in tungsten and the rate of evaporation of thorium were calculated as functions of T and θ'. It was concluded that for values of θ' between 0.2 and 0.8 the rate of evaporation ν_a was approximately independent of θ'.

Subsequent investigations in this laboratory by Dushman and Koller, who worked with hundreds of thoriated filaments from different sources, showed that the apparent diffusion coefficients obtained by the methods already described, instead of being the same for all filaments, depended very greatly on the diameter of the filament and on the size of the crystal grains, being much greater for filaments of a large diameter, and especially for those of very fine grain. Somewhat later Clausing,[3] from experiments with single-crystal thoriated filaments and with thoriated filaments on which crystalline tungsten was deposited, proved that the thorium arrives at the surface mainly along the boundaries of the crystal grains.

In a series of papers J. A. Becker and his co-workers [4, 2] have shown that with monatomic films of barium and cæsium, the logarithm of the electron emission is not strictly a linear function of θ, as is implied by Eq. (3), but that the curve giving log i as a function of σ at a given temperature is concave

[3] P. Clausing, *Physica*, **7**, 193 (1927).
[4] J. A. Becker, *Phys. Rev.*, **28**, 341 (1926).

downwards and shows a maximum at a definite value σ_m. This maximum in the emission at a definite value of σ has also been found by Lukirsky and his co-workers [5] for films of thorium deposited on tungsten. For values of σ greater than σ_m, log i decreases, approaching a constant value before σ/σ_m becomes 2.

Becker and Lukirsky have suggested [4, 5] that the value σ_m corresponds to a complete monatomic film and that the properties of the film undergo no sudden change as the second layer of atoms is being formed. Both for cæsium and for thorium Becker measured the rate of evaporation from the film and found no marked increase in the rate of evaporation as σ increases through the value σ_m.

Within the last few years Dr. J. B. Taylor and I have made accurate determinations [6] of σ for cæsium films adsorbed on tungsten, and we have measured ν_a, ν_p and ν_e (the rates of evaporation of atoms, positive ions and electrons) as functions of T and σ. The existence of a maximum value of ν_e at a definite value σ_m has been confirmed but it was found that σ_m is only 0.67 σ_1. In other words, the maximum electron emission occurs at $\theta_m = 0.67$. Although there is no unusually rapid increase in ν_a as θ increases through θ_m, ν_a tends to increase almost discontinuously as θ approaches unity corresponding to a value of $\sigma_1 = 3.56 \times 10^{14}$ atoms cm.$^{-2}$ (1 Cs atom for every 4 W atoms).

The frequent occurrence of monomolecular adsorbed films and their stability is primarily due [10] to the fact that the crowding of the atoms in a monatomic film when the surface concentration reaches a limiting value must result in a marked increase in the rate of evaporation of *atoms*. There is, however, no theoretical reason why the number of *electrons* emitted should vary discontinuously as σ passes through the value of σ_1.

Becker [2, 7] has found that barium, cæsium and thorium can diffuse over the surface of a tungsten filament at high temperatures. The diffusion of thorium on tungsten was also observed by Lukirsky et al.[5] Thus, if a film of these

[5] P. Lukirsky, A. Sosina, S. Wekschinsky and T. Zarewa, *Zeit. f. Physik*, **71**, 306 (1931).

[6] J. B. Taylor and I. Langmuir, *Phys. Rev.*, **44**, 423 (1933).

[7] W. H. Brattain and J. A. Becker, *Phys. Rev.*, **43**, 428 (1933).

substances is formed on one side of the filament, it distributes itself uniformly over the filament, if the filament temperature is raised to a value 200° or 300° lower than that at which the adsorbed film shows approximately similarly rapid loss by evaporation. Two methods have been developed [8] for measuring quantitatively the diffusion coefficient of cæsium atoms on a tungsten surface. The diffusion coefficient in cm.^{2} sec.$^{-1}$ for low values of θ was found to be

$$\log_{10} D = -0.70 - 3060/T. \qquad (5)$$

The temperature coefficient corresponds to an activation energy for diffusion of 14 Kg. Cal. per g. atom or 0.6 electron-volt. Brattain and Becker [7] have made a rough measurement of the diffusion of thorium atoms over tungsten at 1655° K. obtaining the value $D = 2.44 \times 10^8$ cm.^{2} sec.$^{-1}$.

Brattain and Becker [7] have recently measured the relationship between log i and σ for thorium films on tungsten. They maintained a filament of pure thorium at a constant temperature and thus vaporized thorium at a constant rate onto a tungsten ribbon which was mounted parallel to the thorium filament. In this way σ was made to increase at a uniform rate and therefore a curve giving log i as a function of time made it possible to determine any departures from linearity in the relation between log i and σ. Unfortunately, however, these experiments provided no absolute measure of the value of σ. Brattain and Becker adopt as a unit in measuring σ the amount of thorium which gives the maximum electron emission at a given temperature. They thus measure σ in terms of the quantity f which is defined by

$$f = \sigma/\sigma_m = \theta/\theta_m. \qquad (6)$$

In my early work [1] I found that the value of θ' is independent of the testing temperature used in its measurement, provided that this temperature is so low that diffusion and evaporation do not alter θ during the measurement. Since i, and i_0 are easily determined experimentally, it is convenient to express the activity of the filament in terms of θ', even though θ' is no longer to be identified with the covering fraction θ.

[8] I. Langmuir, *Phys. Rev.*, 40, 463 (1932).

It was found that for a filament having any given activity, as measured by θ', the emission varies with temperature in accord with the equation,

$$i = AT^2\epsilon^{-b/T}, \tag{7}$$

where b and $\log A$ are independent of temperature, but are both linear functions of θ'. Becker and Brattain have confirmed these conclusions and it is possible from their data to derive the following equations to express these linear relationships:

$$b = 52{,}000 - 18{,}800\ \theta' \text{ degrees} \tag{8}$$

and

$$\log_{10} A = 1.84 - 0.65\ \theta'. \tag{9}$$

The relationship between θ' and f, as found by Brattain and Becker, is given by the first and fourth columns of Table 1. For values of $\theta' < 0.96$, the relationship is well expressed by the empirical equation,

$$\theta' = 1.135\ (1 - \epsilon^{-2.38\ f}). \tag{10}$$

This non-linear relationship between θ' and f is interpreted as being due to a variation of the dipole moment M of the adsorbed thorium atoms. Taylor and Langmuir [6, 9] have found in their studies of cæsium films on tungsten that this decrease in the value of M as θ increases is due to the mutual depolarizing effect of neighboring dipoles.

The new relationship between θ' and f given by Eq. (10) requires that the earlier calculations of diffusion coefficients and of evaporation rates for thorium on tungsten should be revised. Comparing Eqs. (4) and (10) we find

$$df/dt = 0.420\ k(1 - \theta')/(1.135 - \theta'). \tag{11}$$

Thus the factor $(1.135 - \theta')$ in the denominator nearly balances the factor $(1 - \theta')$ in the numerator so that df/dt remains practically constant for a wide range of values of θ'. A large number of activation curves obtained in this laboratory prior to 1923 as well as in recent work, have shown, in accordance with the views of Brattain and Becker that

[9] I. Langmuir, *Jour. Amer. Chem. Soc.*, **54**, 2798 (1932). See especially pp. 2816–2829.

TABLE I.

Properties of Adsorbed Thorium Films on Tungsten. Data calculated for $\theta_m = 0.7$ and $T = 2000°$ K. except as Otherwise Noted. ν Refers to Atom Evaporation in f-units cm.$^{-2}$ sec.$^{-1}$.

1. f.	2. θ.	3. $\sigma \times 10^{-14}$ f-units.	4. θ'.	5. V volts.	6. $10^{13}M$ c.g.s. (e.s.).	7. F dyne cm.$^{-1}$	8. $\log_{10}\frac{\sigma\nu}{f}$.	9. $\sigma\nu$.	10. $10^{-8}E$ volt cm.$^{-1}$	11. D/D_0.	12. $10^7\nu$ at 2000° K., f-units.	13. $10^4\nu$ at 2400° K., f-units.
0.00	0.00	0.0	0.00	0.00	3.90	0.0	0.000	0.000	0.0	1.00	0.0	0.0
0.05	0.035	0.25	0.127	0.173	3.68	7.7	0.105	0.064	5.2	1.25	1.2	2.1
0.1	0.07	0.5	0.240	0.327	3.47	16.8	0.204	0.160	9.6	1.46	3.0	5.1
0.2	0.14	1.0	0.430	0.585	3.10	39.0	0.385	0.485	18.6	1.85	9.1	14.7
0.3	0.21	1.5	0.579	0.788	2.79	65.6	0.550	1.065	26.2	2.20	20.0	31.0
0.4	0.28	2.0	0.697	0.949	2.52	96.1	0.703	2.02	32.3	2.51	38.0	57.0
0.5	0.35	2.5	0.790	1.076	2.28	132.0	0.860	3.62	38.0	2.86	68.0	100.0
0.6	0.42	3.0	0.863	1.175	2.08	174.0	1.024	6.34	42.2	3.24	119.0	171.0
0.7	0.49	3.5	0.920	1.252	1.90	226.0	1.209	11.3	46.0	3.71	212.0	297.0
0.8	0.56	4.0	0.962	1.310	1.74	290.0	1.423	21.2	48.0	4.30	398.0	557.0
0.9	0.63	4.5	0.988	1.345	1.59	377.0	1.697	44.8	50.0	5.13	841.0	1,170.0
1.0	0.70	5.0	1.000	1.361	1.445	502.0	2.066	116.5	50.8	6.35	2,190.0	3,030.0
1.1	0.77	5.5	0.993	1.340	1.30	699.0	2.619	457.0	50.0	8.3	8,600.0	12,000.0
1.2	0.84	6.0	0.966	1.312	1.16	1,069.0	3.600	4,780.0	49.3	12.0	90,000.0	
1.3	0.91	6.5	0.935	1.294	1.04	2,006.0	5.933	1.1×10^7	49.2	21.6		
1.4	0.98	7.0	0.901	1.263	0.93	9,630.0	23.6	6.0×10^{23}	49.0	99.5		
2.0		10.0	0.840	1.18								

df/dt obtained from activation curves remains substantially constant, the observed gradual decrease at high values of f being adequately explainable either by an actual decrease in μ, the rate of arrival of the thorium as the interior supply becomes exhausted, or by evaporation of the thorium which increases rapidly as f increases.

These results indicate that there is at present no physical reason for believing in the reality of induced evaporation. The writer has long felt and Brattain and Becker have clearly pointed out that the original theory of induced evaporation is incompatible with the known mobility of the thorium atoms on the filament at activation temperatures. This mobility also explains how the surface concentration σ can be uniform over the surface even though most of the thorium arrives at the surface along the grain boundaries.

The acceptance of the true non-linear relation between θ' and f has a profound effect on the interpretation of the experimental results on the rates of evaporation of thorium atoms:—whereas the earlier calculations gave values of ν_a that were approximately independent of θ', it is now found from the same experiments that ν_a increases rapidly with f. Between $f = 0.3$ and $f = 0.9$, ν_a is given by the empirical relation,

$$\nu_a = \nu_0 \epsilon^{Hf}, \tag{12}$$

where H is a constant having the value 5.6.

Experiments at different temperatures, which measure the temperature coefficient of ν_a, give for the heat of evaporation, Q, the value:

$$Q_r = 174 \text{ Kg. Cal. per gram atom.} \tag{13}$$

This variation of ν_a with f is in excellent agreement with the data obtained by Brattain and Becker on the evaporation of thorium films from a filament at 2200°; their experiments lead to the value $H = 5.5$ in this same range of values of f.

THEORETICAL RELATIONSHIP BETWEEN ν_a AND ν_e.

It has been shown by Langmuir and Taylor[9, 6] that ν_e and ν_p can be calculated from ν_a for the case of cæsium films on tungsten. I now wish to show that similar calculations

enable us to determine the variation of ν_a with f for thorium atoms from our knowledge of the relation between ν_e and f.[10]

The basis of such calculations is as follows: The Boltzmann equation,

$$\nu_e/\nu_w = \exp.\ (Ve/kT), \tag{14}$$

enables us to calculate the contact potential V from the ratio of the electron emission ν_e of the thoriated filament to ν_w, that of a pure tungsten filament at the same temperature. Combining Eqs. (3), (7), (8), (9) and (14), the contact potential is found to be

$$V = (1.62 - 1.29 \times 10^{-4}\, T)\theta' \text{ volts}. \tag{15}$$

The values of V calculated from θ' in this way for $T = 2000°$ are given in column 5 of Table 1.

The contact potential is related to the dipole moment M of the individual adatoms by the relation,

$$V = 2\pi\sigma M. \tag{16}$$

In order to calculate M from V we must know the absolute value of σ. For this purpose we shall make the provisional assumption that

$$\theta_M = 0.7. \tag{17}$$

This is approximately the value that has been indicated by experiments on cæsium films. From the general similarity of the curves of θ' as a function of f for barium, thorium and cæsium, it seems reasonable to assume that θ_m is not materially different in these three cases. We shall subsequently discuss what effects would be produced by an alteration of the value of θ_m. From this value of θ_m and the value of σ_1 we have therefore

$$\sigma = 5.0 \times 10^{14} f. \tag{18}$$

Using these values of σ and V in e.s. units, we may now calculate by Eq. (16) the values of M (in c.g.s. e.s. units) which are given in Table 1, column 6. The dipole adatoms repel one another with a force K given by

$$K = (3/2)M^2/r^4, \tag{19}$$

[10] A review of the theory of these relationships was given in the Nobel lecture, Les Prix Nobel en 1932, reprinted in *Chem. Revs.* for October 1933, and in *Angewandte Chemie*, 46, 719 (1933), in German.

where r is the distance between two dipoles. Taking into account this force between adatoms and also the short range forces which prevent any two atoms from occupying the same space at the same time, the following general 2-dimensional equation of state for dipole atoms adsorbed by a metallic surface was derived:[9]

$$F = \sigma kT/(1 - \theta) + 3.34\sigma^{5/2}M^2 + 1.53 \times 10^{-5}\sigma^2 T^{1/3} M^{4/3} I, \quad (20)$$

where I is an integral whose numerical value, which can never exceed 0.89, can be obtained by tables and curves from the values of M, σ and σ_1. This equation which was derived for the study of cæsium films on tungsten should be applicable also to thorium films. The quantity F is the spreading force (dynes cm.$^{-1}$) which is the analogue in a 2-dimensional system of the pressure in a 3-dimensional system.

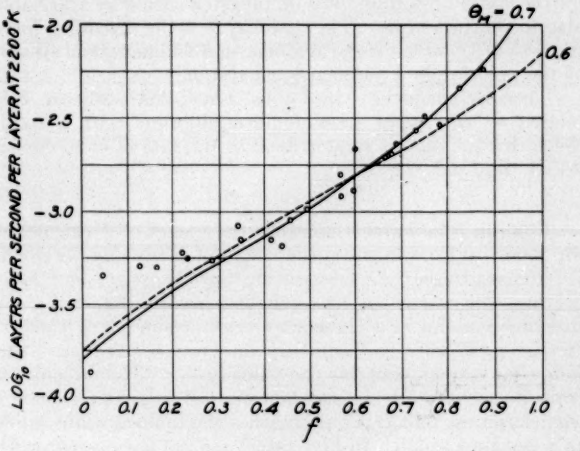
Thermodynamically, by Gibbs' adsorption isotherm, F is related to the vapor pressure in equilibrium with a solid. Since this pressure is proportional to the rate of evaporation ν_a, we may put

$$dF/d(\ln \nu_a) = \sigma kT. \quad (21)$$

Column 7 in Table I contains the values of F calculated for 2000° by Eq. (20) from the values of M already obtained. By differentiating F, substituting into Eq. (21) and integrating, the values of $\log_{10}(c\nu_a/f)$ may be obtained as a function of σ and T. These are given in column 8 of Table I. Here c represents the arbitrary integration constant. The following column contains the value of $c\nu_a$. The integration constant used in calculating the values of $c\nu_a$ given in Table I was chosen so that $c\nu_a/f$ approaches the limiting value unity as f becomes small. In Fig. 1 the values of $\log_{10}(\nu_a/f)$, with an arbitrary constant added, have been plotted against f. The small circles give Brattain and Becker's experimental data[7] of the evaporation rates at 2200°, as shown in Fig. 16 of their paper. The dotted curve in Fig. 1 has been calculated in the same manner as the data in Table I, but using $\theta_m = 0.6$. The data agree much better with the value 0.7. Brattain and Becker, in their Fig. 16, have ignored the lowest experimental point and have drawn through their points a parabola

having a horizontal tangent at $f = 0$. This parabolic form of curve would require that M should increase with f, whereas the electron emission proves that it decreases as f increases. If more weight is attached to the lowest point, this difficulty disappears but the accuracy of their data below $f = 0.2$ becomes doubtful. These theoretical values of ν_a/f with $\theta_m = 0.7$ are in practically complete agreement with our own experimental determinations of the rates of evaporation of thorium from thoriated filaments with temperatures ranging from 2200° to 2400° K. The experimental evidence will be published separately.

FIG. 1.



Similar calculations to those involved in Table I but for 2400°, show only very slight changes in the shape of the curve giving ($\log \nu_a/f$) so that the agreement between Becker's determinations at 2200° would remain unchanged if the calculations had been made at 2200° instead of at 2000°.

Column 10 of Table I gives the depolarizing field, E, acting on any adatom as the result of the presence of its neighbors. This field has been calculated by the equation:[9]

$$E = (8/3\sigma_1)[F - \sigma kT/(1 - \theta)]/\theta M. \qquad (22)$$

It is seen that these forces are of enormous magnitude: about 10^7 volts per cm. at $f = 0.1$. It is not surprising that field strengths as great as these would tend to push the charged adatoms down close to the tungsten surface and thus decrease the dipole moment. It is probable that the distance from a tungsten surface at which a cæsium atom or thorium atom is in equilibrium is determined by the pressure gradient in an electron atmosphere which extends an appreciable distance beyond the atoms of the metal. Since the electron shells of the adatoms may be considered to be impervious to the Fermi electrons,[11] there must be a much greater pressure exerted by the electrons on the portion of the shell which lies closest to the underlying metal. It is hoped in future work to develop this theory quantitatively.

DEPENDENCE OF SURFACE DIFFUSION COEFFICIENT ON θ.

If there are no forces acting between adatoms, the diffusion coefficient [6] for surface migration is given by $d = a^2/4\tau$ where a is the lattice constant of the elementary spaces in which the adsorbed atoms can arrange themselves, and τ is the average life of an adatom in any one elementary space when the neighboring spaces are vacant. The life τ depends upon the energy barrier between adjacent elementary spaces. For cæsium on tungsten it is about 0.6 volt which is about 21 per cent. of the heat of evaporation of adatoms.

If there are repulsive forces acting between the adatoms then, when there is a concentration gradient, there is a net force acting on every adatom tending to make it move towards a region of lower concentration. This force can be calculated by a process analogous to that which we used in calculating F from K by Eqs. (19) and (20). It is thus found that the force K acting on a given adatom is

$$K = 2(d\sigma/dx)(F - \sigma kT)/\sigma^2. \qquad (23)$$

By taking this force into account it is seen that the heights of the barriers on the opposite sides of a given elementary space are different. The probability of the passage over the two

[11] O. K. Rice, *J. Chem. Phys.*, 1, 649 (1933).

barriers can be estimated by the Boltzmann equation. In this way it is found that the diffusion coefficient is given by

$$D = D_0[(2F/\sigma kT) - 1]. \quad (24)$$

For very low values of θ, D thus becomes equal to D_0. The values of D/D_0 are given in column 11 of Table 1. It is seen that the surface diffusion coefficient is over six times as great for $F = 1$ as it is for very low values of F. Theoretically F must increase extremely rapidly as θ approaches unity. A variation of this kind was observed in the migration of cæsium on a tungsten surface. Brattain and Becker found a similar increase in thorium on tungsten. They suggested that the increase was due to partial evaporation of the thorium from the tungsten surface, the atoms, however, not being able to escape from the surface.

Although from the foregoing equations both ν_a and D depend upon F, it does not appear to be a useful concept to regard the effect of concentration on D as being due to partial evaporation. If the migration over the surface were due mainly to the hopping of atoms between adjacent spaces in such a way that the atoms resembled gas atoms, then it would seem that the migration of cæsium from the surface would be markedly increased by surrounding the filament with a strongly negatively charged cylinder which would allow the adsorbed positive ions to rise to greater heights above the surface. The effect of such external fields on the diffusion coefficient was found to be negligible.

ANALYSIS OF EXPERIMENTAL ACTIVATION AND DEACTIVATION CURVES.

In transient states of the adsorbed films corresponding to activation and deactivation curves, the rate of change of the surface concentration σ depends upon the balance between μ, the rate of arrival from the interior, and ν, the rate of evaporation from the surface. Thus we have

$$\sigma_m df/dt = \mu - \nu. \quad (25)$$

Since σ_m has not yet been directly determined experimentally for thoriated filaments, it is useful and convenient to use as a unit in measuring the amounts of thorium that diffuse or evaporate, the quantity represented by σ_m. Let

us call this a f-unit, for this is the amount of thorium which will cover a unit area of tungsten surface to such a degree that the surface has the maximum electron emission at a given temperature. Thus if we express μ and ν in f-units, Eq. (25) becomes

$$df/dt = \mu - \nu. \tag{26}$$

When a filament is activated at a low temperature such as 1900 or 2000°, ν is usually negligible compared with μ except possibly at the highest values of f. Thus an experimental determination of df/dt leads directly to the value of μ. The experimental studies prior to 1923 showed that the value of μ at a given activating temperature depended greatly on the temperature and duration of the flashing to which the filament had been previously subjected. By adopting a standing flashing procedure, such as heating the filament for 3 minutes at 2800°, the filament can be brought into a condition in which μ has a definite value at a given temperature. By measuring μ at a series of different activation temperatures, the temperature coefficient can be determined. The logarithm of μ plotted against $1/T$ gave a straight line whose slope corresponds to the heat of diffusion of Q_μ = 90 Kg. Cal. per gram atom.

When the filament is heated to 2300° or more, ν usually exceeds μ when the filament is in a very active condition. that is, for high values of f. From the values of μ determined by an activation curve at lower temperatures and from the known temperature coefficient of μ, we can calculate a value of μ to use in Eq. (26) when applied to a deactivation curve, and in this way from experimental values of df/dt at different values of f we should be able to determine ν as a function of f and t.

These values of f should presumably be independent of the reserve supply of thorium in the interior of the filament which must determine the absolute magnitude of μ. Thus if during flashing we adopt different temperatures such as 2700° and 3000°, we obtain, from activation curves at lower temperatures, values of μ which differ greatly, although the temperature coefficients of μ obtained by using different activation temperatures remain unchanged.

If we determine values of ν_a as a function of f and T, by a series of deactivation curves, for filaments which have previously been flashed at different temperatures, we find that the values of ν_a differ greatly according as different flashing temperatures are used. On the other hand, if we place $\mu = 0$ in Eq. (26), and then calculate ν by the relation $\nu = -df/dt$, we usually obtain values which are strikingly independent of the reserve thorium supply. They also prove to be the same for thoriated filaments of different crystalline structures, in spite of the fact that the values of μ at a given deactivation temperature and flashing temperature vary greatly with grain size.

The values of ν obtained in this way not only from the 1922 experiments but also from data of more recent experiments kindly furnished me by Dr. G. R. Fonda [12] give curves for log ν_a as a function of f at the deactivating temperature of 2400° that agree remarkably well with a curve prepared from the data of column 13 of Table I which were obtained from values of $c\nu_a$ calculated for 2400° (by the method used to get the data of column 9) by taking $c = 296$. When these experimental data for ν_a are plotted as in Fig. 1, they show even better agreement with the theoretical curve than do Brattain and Becker's data, and they show no tendency to flatten out at low values of f as the latter do.

From deactivation curves at various temperatures the temperature coefficient of ν_a was found. For each temperature a value of the integration constant c was chosen to give best agreement with the experiments. The values of log c when plotted against $1/T$ gave a straight line corresponding to

$$\log_{10} c = -13.78 + 39{,}000/T. \qquad (27)$$

Thus at 2000°, $c = 5.25 \times 10^5$. With this value and the data for $c\nu_a$ in column 9 of Table I, the values of ν_a in column 12 were calculated. These are in f-units; they may be con-

[12] These data were from the experiments described by G. R. Fonda, A. H. Young and A. Walker, *Physics*, 4, 1 (1933). In the published paper the data were analyzed in terms of the older theory in which θ' was identified with θ. The recalculations referred to were made from the original experimental measurements of i which were not given in the published paper.

verted to atom evaporation rates by multiplying by $\sigma_m = 5.0 \times 10^{14}$. From the temperature coefficient of ν_a the heat of evaporation Q_ν is found to be 178 Kg. Cal. at $f = 0$, 174 at $f = 0.5$ and 172 at $f = 1.0$.[13]

Only when the reserve supply of thorium was made low by long heating at such a temperature as 2300° was it possible by the foregoing method to determine ν down to very low values of f. The experiments show that with higher reserves of thorium and especially with coarse grained filaments μ was not actually zero, although it always had a very low value compared to that which would be calculated by the known temperature coefficient from values of μ obtained during activation curves.

After obtaining convincing evidence that ν is actually an intrinsic property of the adsorbed thorium film which depends only on f and T, the following procedure was adopted in analyzing deactivation curves: From the experimental data giving i as a function of t, θ' was calculated by Eq. (3); then from Eq. (10) and columns 1 and 4 of Table 1, f was determined as a function of t. From this curve the values of df/dt were obtained and ν was found from column 13 of Table 1 from f or θ'. By substituting these into Eq. (26) μ was thus calculated. The data supplied by Dr. Fonda proved to be particularly illuminating.

During each deactivation run μ decreased in accord with an equation of the type,

$$\mu = \mu_R + \mu_0 \epsilon^{-\alpha t}. \tag{28}$$

The steady value μ_R, which was the limit approached after a long time (usually after several hours at 2400°), was interpreted as being due to the continuous generation of thorium within the filament by a reduction of the thorium oxide. The value μ_0, thus represented the reserve supply of thorium which had accumulated in the filament by the preliminary flashing at high temperature. The coefficient α is thus determined by the rate of loss of thorium by diffusion from the interior.

[13] In the 1923 paper (Ref. 1) Q_ν was given as 204 Kg. Cal. which, from various considerations, must be regarded as too high for it exceeds even that of tungsten in spite of the fact that thorium evaporates from the surface of a filament far more rapidly than tungsten does. The new values of Q_ν agree well with that obtained (177 Kg. Cal.) by Mary R. Andrews (*Phys. Rev.*, 33, 454 (1929)).

DIFFUSION ALONG GRAIN BOUNDARIES AND THROUGH CRYSTAL GRAINS.

The earlier unpublished work of Dushman and Koller, and particularly the clean-cut experiments of Clausing [3] have demonstrated the importance of grain size on the rate of arrival μ of thorium at the surface of the filament. It seems reasonable to assume, therefore, that a large fraction of the thorium which arrives at the surface travels from the interior along grain boundaries, and then spreads over the surface. This seems to be the proper interpretation of the normal activation curves, and thus the values of μ which are obtained from these activation curves measure primarily, not the true diffusion through solid tungsten, but the rate of arrival along grain boundaries. This conclusion is supported by the observation of Fonda, Young and Walker, given in their Table 3, that the activation constant and therefore μ, by Eq. (11), decreases greatly as the grain radius increases. Thus as the grain radius increased from 4 to 8.6 microns, the value of μ decreased 70 per cent.

The values of μ obtained from the deactivation curves at 2400° showed entirely different behavior; they increased as the grain size increased, and in all cases were very small compared with the values extrapolated from the activation curves at lower temperatures. We must therefore conclude that at temperatures as high as 2400° the thorium which arrives at the surface by migration along grain boundaries does not spread over the free surfaces of the grains, but instead evaporates without contributing appreciably to the electron emission. Since the temperature coefficient ($Q_v = 174$) of the evaporation rate is large compared to that of the diffusion coefficient of surface migration (probably about $Q = 66$, see below), it would at first sight appear reasonable that at high temperatures evaporation should increase so much more rapidly than surface migration that the thorium would evaporate before it can migrate very far from the grain boundaries. We shall see later, however, that there are theoretical difficulties involved in this interpretation. In any case, whether or not we are able to give a theoretical explanation, it seems necessary to recognize definite experimental evidence that at 2400°, and to a lesser degree at

2300°, the thorium that migrates along boundaries does not contribute to the activity θ'.

The values of μ_0 of Eq. (28), obtained by deactivation curves at 2400°, appear to be determined by the diffusion of thorium from the interior through the homogeneous crystal grains. The study of data from numerous experiments has led to the following theory of the mechanism by which thorium is brought to the surface.

The work of Jeffries [14] and others has shown that after the thoriated filament has been heated to a high temperature, the thoria exists in the form of fine spherical particles which are distributed throughout the whole volume of the filament. Although the grains are apt to be closer together along the grain boundaries of the crystals, the larger part of the whole thoria content usually lies within the crystal grains unless the crystal grains are of unusually small size. By heating to very high temperatures Jeffries has found that the large particles of ThO_2 increase in size and the small ones tend to disappear proving that both thorium and oxygen can migrate through the crystals.

It has been shown by Koref and Reiter [15] that when a thoriated filament is heated for 1000 hours at 2400° in high vacuum, the thoria gradually disappears from the outer layers and the tungsten grains in these outer layers increase in size, although those in the interior of the crystal remain unchanged. A minute external pressure of oxygen, such as that produced by the presence of saturated vapor of phosphorus pentoxide at room temperature entirely prevents this loss of thoria from the filament and also prevents the grain growth.

Recently in some studies of the effects of oxygen on tungsten filaments which Dr. J. B. Taylor and I have been carrying out, we have found that when a tungsten filament is heated at 1800° K. for 30 minutes in a pressure of oxygen as low as 4×10^{-7} baryes the oxygen penetrates deeply into the tungsten filament so that after the surface is cleaned by

[14] Zay Jeffries, Paper No. 1614-E, *Trans. Amer. Inst. Min. and Met. Engs.* (1927).

[15] F. Koref and C. Reiter, *Zeit. f. Tech. Phys.*, **6**, 359 (1925) and *Tech.-Wiss. Abhandl. aus dem Osram-Konzern*, **2**, 99 (1931).

momentarily flashing at 2400° and the filament is brought to 1600°, the electron emission progressively decreases by the diffusion of oxygen from the interior of the filament. This phenomenon is being studied in great detail, but only preliminary data are yet available.

From these results and those of Koref and Reiter it thus appears that thorium oxide dissociates into thorium atoms and oxygen atoms which then exist in the filament in solid solution. There is thus presumably an equilibrium given by the equation,

$$ThO_2 \rightleftarrows Th + 2O.$$

The higher the temperature, the greater the partial pressure of the thorium and the oxygen. The law of mass action would indicate at any temperature that

$$[Th] \times [O]^2 = \text{const.} \qquad (29)$$

The oxygen apparently diffuses through the body of the filament (not preferentially along the grain boundaries) at a rate far faster than the thorium. The oxygen also evaporates from the surface at a rate much higher than the rate of evaporation of thorium. Thus by flashing a filament at high temperature, the diffusion of the oxygen leaves a concentration of oxygen which decreases from a maximum at the center to a negligibly small value near the surface of the filament. If the equilibrium implied by Eq. (29) is attained, the thorium concentration must then be a minimum near the axis of the filament and rise to relatively very high values at a short distance from the surface. Thus thorium diffuses from this region of maximum concentration at a relatively rapid rate toward the surface and at a lower rate toward the axis. This must cause just such a removal of thoria from the outer layers as is observed from the experiments of Koref and Reiter. The original thorium production thus takes place regardless of grain boundaries.

The loss of oxygen results in the production of a surplus of thorium, having this peculiar distribution, every time the filament is flashed at high temperature.

When the filament is brought to a lower temperature, this reserve supply of thorium diffuses from the interior of the crystal grains to the crystal boundaries, and then migrates at

a relatively high rate along the crystal boundaries to the surface. As a first approximation, at least, we may assume that the resistance to diffusion, corresponding to grain boundaries, is negligible compared to that of diffusion from the interior of the grains. Thus the rate at which each grain loses thorium is the same as though that grain were in free space, i.e., so situated that all thorium that reaches any of its faces can immediately evaporate.

In the first paper on thoriated filaments [1] it was shown that the laws of diffusion from the interior of a cylinder should cause an exponential decrease in the value of μ at the surface corresponding to the last term in Eq. (28). The value of α for cylinders was shown to be

$$\alpha = 5.78\, D/R^2, \tag{30}$$

where R is the radius of the filament. We now see, however, that the radius of the filament is not the determining factor —it is, rather, the average radius of the grains.

For diffusion within spheres in place of Eq. (30) we should have

$$\alpha = \pi^2 D/R^2. \tag{31}$$

The grains that we have to deal with, although fairly regular are by no means spheres, so we can merely guess at the radius. A reasonable value would seem to be

$$R_s = 0.75\, R_g,$$

where R_g is the apparent average radius of the grains shown by microscopic examination. From the experimentally determined values of α we may thus calculate the diffusion coefficient,

$$D = 0.057\, R_g^2 \alpha, \tag{32}$$

where R_g is the grain radius.

An analysis of Fonda's data has shown, in fact, that the values of D obtained in this way by using the grain radius instead of a filament radius are independent of the grain size. The average value at 2400°,

$$D = (1.0 \pm 0.2)10^{-11}\ \text{cm.}^2\ \text{sec.}^{-1} \tag{33}$$

The reason that μ_0 (and also μ_R) increases as the grain

size increases is presumably the fact that the surface at which the thorium concentration is a maximum lies at a depth below the filament surface which is greater than the grain radii used in these experiments (8.6 microns radius). Thus the amount of thorium stored within the surface grains increases rapidly as the size of the grains increases. On the other hand, this increase does not continue with very large grain, as, for example, in Pintsch wire.

The total amount of stored thorium which reaches the surface of the filament through the surface grains can be obtained by integration of Eq. (28). If we call S the total amount per unit area of filament surface expressed in f-units, we have

$$S = \mu_0/\alpha. \tag{34}$$

The experimental data indicate that for fine grain filaments ($R_g = 4$ microns) S is only 0.4 f-unit, whereas with the filament having grains of 6.9 microns, S has risen to 4.8. With the filament having very coarse crystals (1 mm. long) S rose to 77. This is in accord with the fact that with large crystals, all thorium must diffuse to the surface through the crystals, whereas with fine grain filaments a large part reaches the surface by migration along grain boundaries and is there lost by evaporation.

A large number of the conclusions drawn in this paper are in accord with the researches of Lukirsky, Sosina, Wekschinsky and Zarewa.[5] These investigators have found the maximum in the emission corresponding to a definite value σ followed by a constant emission at a value of approximately $f = 2$. They have also demonstrated the importance of mobility over the surface. In some other respects, however, the conclusions they drew are in variance with those given here. They concluded that the rate of evaporation from a complete monatomic film should be less than that from a partially covered surface. They also believe that they observed, for surfaces having a low surface concentration, that there is a considerable rate of evaporation at 1570° K., although at a somewhat higher temperature of 1700° K., there was no measurable evaporation. A careful study of their paper leads me to suggest that the decrease in emission that was observed at 1570° K. was not due to evaporation,

but to migration from one side of the filament to the other. They had, in another experiment, found that migration caused an increase in emission and were therefore not prepared to interpret a decrease in a similar manner. An examination of the curves of ν_s as a function of f (see Table I) shows that only for values of f greater than 0.73 does an equalization of the surface concentration by migration cause an increase in emission. Below this value of f, migration causes marked decreases in emission. Not only the shape of the curve but also the magnitude of the temperature at which this effect was first observed indicates that it was a typical effect of migration.

The conclusion that evaporation from very dilute films takes place more rapidly than from concentrated films seems to have been based largely on their interpretation of this experiment. It seems to me that the characteristic behavior of the monatomic film indicates that such a film must have a far higher rate of evaporation than the less concentrated films.[10] It is shown by Becker's work and by our results in Table I that this increase amounts to a factor of about 70-fold as f increases from 0.1 to 1.0.

ABSOLUTE VALUES OF DIFFUSION COEFFICIENTS.

Brattain and Becker, from experiments on the change in electron emission as thorium migrates from one side of a filament to another, have calculated the following values for the surface diffusion coefficient for thorium atoms on tungsten. At $T = 1535°$ K., $D = 1.84 \times 10^{-9}$ and at 1655°, $D = 2.44 \times 10^{-8}$. This calculation, however, is based on the assumption that D is independent of f. The range of f used in these experiments was very large. The original deposition on the front side of the filament corresponded to $f = 1.77$, whereas $f = 0$ on the other side. At the end of the experiment f had reached the value 0.88 on both sides. They conclude from an analysis of the curves that the diffusion coefficient must vary considerably as f changes by a factor of at least 2 or 3 in their experiments. An examination of their curves shows that the initial rate of change was at least 10 times the average rate of change. Examining the data of column 11 of Table I we see that D/D_0 increases enormously

rapidly as f approaches 1.4, being about 12 times as great as at $f = 1.0$. The very high initial rate observed in Brattain and Becker's work thus lends support in our theoretical conclusion that D approaches very high values as θ approaches unity. In the future Brattain and Becker's method should be applicable to accurate determinations of D. For this purpose, however, after placing a film on one side, it should be allowed to equalize over the surface and then, with a second deposition of thorium, a moderate change in f should be made on one side and the subsequent changes in electron emission observed. In this way only a small range in the values of f will be covered in any one experiment, so that the convenient assumption of a constant value of D will be justified.

From the two values of D given by Brattain and Becker they calculate the heat of diffusion as $Q = 110$ Kg. Cal. This value is so high as to be entirely out of line with other known values for diffusion coefficients. Dushman and Langmuir [16] proposed as a universal equation for adsorption in crystalline solids,

$$D = (Q/Nh)a^2\epsilon^{-Q/RT}, \tag{35}$$

where N and h are respectively the Avogadro and the Planck constant, and a is the spacing between atoms in the crystal. Inserting numerical values this becomes

$$D = 1.05 \times 10^{10}\, Qa^2\epsilon^{-Q/2T}, \tag{36}$$

where Q is expressed in gram calories per gram atom.

For the migration of cæsium on tungsten, as given by Eq. (5), we have $Q = 14{,}000$ g. cal. Inserting this in Eq. (36) we obtain

$$\log_{10} D = -0.39 - 3060/T, \tag{37}$$

which agrees excellently with the experimental data represented by Eq. (5).

In Brattain and Becker's experiment which gave $D = 2.44 \times 10^{-8}$ at 1655°, the average value of f was about 1.1. To get D_0 we should divide by 8.3, the value of D/D_0 from Table 1, giving $D_0 = 3.0 \times 10^{-9}$. Examination of Eq. (24)

[16] S. Dushman and I. Langmuir, *Phys. Rev.*, **20**, 113 (1922).

shows that the temperature coefficient of D which determines Q is almost wholly dependent on D_0 and not on the factor in brackets. Taking this value of D_0 and choosing a value of Q which satisfies Eq. (36) we obtain $Q = 66.4$ Kg. Cal. instead of the value 110 given by Brattain and Becker. With the value $Q = 66.4$ we find for the surface diffusion coefficient of thorium on tungsten:

$$\log_{10} D_0 = -0.33 - 14{,}500/T. \tag{38}$$

If, on the other hand, we had used $Q = 111$, then in order to obtain $D_0 = 3 \times 10^{-9}$ at 1655°, the constant term in Eq. (38) would have had to be 5.8 instead of -0.33.

A recent paper by G. E. von Hevesy [17] records tests of Eq. (35) for all known cases of diffusion through homogeneous crystalline media and finds that it is in substantial agreement with experimental data. It would seem, therefore, that Becker's high value for Q is incompatible with our present knowledge of diffusion phenomena. Since Becker's available data are very meager, it is therefore preferable to use Eq. (38) for calculation of the surface diffusion coefficient of thorium on tungsten rather than depend on extrapolations from Brattain and Becker's data by using $Q = 110$.

Taking the value of D given by Eq. (33) for the volume diffusion coefficient of thorium in tungsten crystals at 2400° K., we calculate from Eq. (36) that $Q = 120$ Kg. Cal., giving

$$\log_{10} D = 0.0 - 26{,}200/T. \tag{39}$$

Eq. (36) should presumably be applicable also for the diffusion along grain boundaries for which we have found $Q = 90$ Kg. Cal. Eq. (36) then gives

$$\log_{10} D = -0.13 - 19{,}700/T. \tag{40}$$

The grain boundary presumably consists of a region between two crystals where the lattice is markedly deformed. Let us assume that the thickness b of this boundary is 10^{-7} cm. Then we find

$$\rho = Db(dn/dr), \tag{41}$$

where ρ is the rate of arrival of thorium in f-units per cm. of

[17] G. E. von Hevesy, *Zeit. f. Elektrochem.*, **39**, 490 (1933).

length of the grain boundaries which reach the surface. Experiments on the rate of activation at 2050° with a filament having grains of radius of 4 microns gave $\mu = 1.15 \times 10^{-4}$ f-units cm.$^{-2}$ sec.$^{-1}$ from which we estimate $\rho = 4.6 \times 10^{-8}$ f-units cm.$^{-1}$ sec.$^{-1}$. The diffusion coefficient for grain boundaries at 2050°, by Eq. (40), is 1.8×10^{-10}. Inserting these and the value for b in Eq. (41) shows that dn/dr should be 2.6×10^{9} f-units cm.$^{-4}$. This concentration gradient along the grain boundary would be attained if the concentration along the grain boundary at a depth of 4 microns exceeds that at the surface by only 1 thorium atom per hundred tungsten atoms.

THEORY OF MIGRATION FROM CRYSTAL BOUNDARIES.

The experiments indicate that at 2300° and 2400° the thorium that reaches the surface along grain boundaries evaporates without contributing appreciably to the measured values of θ' and f. That this thorium actually arrives at the surface and leaves it by evaporation is proved by the rapid loss of the reserve supply of thorium with fine grain filaments as indicated by the high values of α in Eq. (28) observed with such filaments. The following analysis allows us to estimate the rapidity with which thorium should spread over the surface under the combined influences of surface diffusion and evaporation.

Within reasonably wide ranges of f from 0.3 to 0.9 the variation of both ν and D can be represented by

$$\nu = \nu_1 \epsilon^{Hf} \quad \text{and} \quad D = D_1 \epsilon^{Kf}, \tag{42}$$

where $H = 5.6$ and $K = 1.4$

Now in a steady state the migration of thorium over a surface from a crystal boundary (assumed to be a straight line) is given by

$$\frac{d}{dx}\left(D \frac{df}{dx} \right) = \nu. \tag{43}$$

By introducing the values of D and ν from Eqs. (42) and assuming that ϵ^{Hf} is large compared to unity, it can be shown that the major part of the concentration drop from f_0 at the crystal boundary to $f = 0$ at a large distance, takes place

within a distance x_0 given by

$$x_0 = \pi[4D_1/\nu_1(H - 3K)]^{1/2}. \qquad (44)$$

Thus if x_0 is small compared to the grain radius R_g, the thorium which migrates from the boundary will not affect the surface concentration except in a narrow region close to the grain boundary. The proper value of ν_1 at 2400° K. can be found by plotting on semi-logarithmic paper the data for ν in column 13 of Table I and extrapolating the best straight line back to $f = 0$. This gives $\nu_1 = 5.8 \times 10^{-9}$.

The value $D_1 = 6.0 \times 10^{-7}$ is found from a similar plot using D/D_0 from column 11, together with $D_0 = 4.3 \times 10^{-7}$ at 2400° from Eq. (38). In this way Eq. (44) gives $x_0 = 0.17$ cm. To get a value of x_0 of 1 micron would require a value $D = 2 \times 10^{-13}$ which is far less than was observed at 1535°.

If we know the rate of arrival ρ in f-units per cm. we may calculate another relation,

$$\rho^2(H - K)^2 = 2\nu_1 D_1(H - 3K)\epsilon^{(H+K)f_0}, \qquad (45)$$

where f_0 is the value of f_0 at the grain boundary. From the observed value of $\rho = 4.6 \times 10^{-8}$ at 2050° found for a fine grained filament ($R_g = 4$ microns) we estimate $\rho = 1.1 \times 10^{-6}$ at 2400° by Eq. (40). This equation shows that D_1 would have to be of the order of 10^{-11} in order to give large values of f_0 for which the equations are applicable.

Thus we cannot explain from these theories the failure of the thorium to migrate out from the crystal boundaries at high temperatures. It seems as though there must be a peculiar structure just at the grain boundary which does not conform to our assumptions. This might produce a kind of resistance to diffusion, or more probably, the evaporation rate of the thorium atoms from the disturbed lattice is enormously higher than from the normal crystal surface.

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An Efficient Pacifier.—According to W. G. Campbell, Chief of the Federal Food and Drug Administration, the use of so-called soothing syrups for infants and young children has materially decreased during recent years, but there are still some potentially dangerous ones on sale. Thus "Sirop d'Anis Gauvin Compound," a remedy apparently well-known in many parts of New England, was found to contain morphine. An investigation showed it to be largely used by mothers working in textile mills who would dose their young children with the "Compound" in the morning before going to work in order to keep them quiet. Upon returning from work at noon they would give their children another dose of the nostrum. An interstate shipment of this product was seized because the label bore false claims for the cure or treatment of bronchitis and other diseases of infants and young children.

C.

Broadcasting Ammonia.—(*Science Service.*) Two University of Michigan physicists, Drs. C. E. Cleeton and N. H. Williams, are using the shortest radio waves ever produced by radio tubes. These waves are less than a half inch long as compared to the previous low of well over an inch and to the commonly used radio waves of about 1500 feet.

The anodes or positive plates of the tubes are made from graphite cylinders only three-tenths of an inch in diameter. The wavelength of the radio waves depends upon the time it takes the electrons to travel from the filament located in the center to the inner walls of the cylinder. The whole vacuum tube is placed in a strong magnetic field. The stronger it is, the shorter the waves.

However, these two physicists did not stop at merely producing the ultra-short waves. The waves were passed through a rubberized cloth bag full of ammonia gas which absorbed a certain wavelength of the wave-band to an abnormal degree. Calculations based upon the wave-length absorbed indicate that one hundred million ammonia molecules in a chain would be only 3½ inches long.

C.

AN ATMOSPHERIC DUST RECORDER.

BY

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SUMMARY.

An apparatus is described for recording general atmospheric dust. The full-scale range of the present model of approximately 120×10^6 particles per cubic foot of air may be increased or decreased as desired. The dust concentrations measured are far below smoke concentrations. The method is to impinge dust on a slowly moving strip of transparent film, and to measure the deposit by a comparison of two beams of light, one passing through the dusty film, the other through clean film. The decrease in transmitted light due to the dust is balanced automatically by a motor-driven optical wedge in the unobstructed beam. The position of this wedge is recorded on a chart. Dusty air is sampled continuously for long periods. Rapid fluctuations of a few minutes in length are registered. In this, and in the fact that it is direct-reading, without tedious laboratory quantitation, the recorder offers distinct advantages over the present dust determinators, almost all of which take momentary samples. A different calibration is needed for different dusts. The machine may be adapted to laboratory or field use. In factories, auxiliary blowers may be operated through relays, when the dustiness exceeds a specified level.

The estimation of dust, fume and smoke concentrations in air is an important factor in evaluating working conditions in factories and mines. Gradually there are being gathered data on permissible dustiness—dust concentrations which, if exceeded, may induce certain respiratory diseases such as silicosis. While these limits are often only approximate, they are of great help to the engineer or plant manager installing or operating dust control equipment designed to give adequate protection to those exposed. The measured atmospheric dust concentrations, expressed in number or weight of particles per unit volume of air, are his only practical guide in appraising conditions.

Of the accepted instruments for dust estimation, none gives a direct-reading, continuous record, at the same time preserving the sample. In fact, none gives a sample which may be measured without tedious, painstaking work in the

laboratory. None rapidly follows changes in dust concentration such as frequently occur in factories and mines.[1] None attempts to control automatically the dust concentration, as, for example, by operating auxiliary exhaust fans.

The recorder to be described eliminates these handicaps, after it is once calibrated for a given dust by a standard instrument of air analysis, such as the Greenburg-Smith impinger (1).

The recorder can be used in industrial plants to measure and control atmospheric dust inhaled by the workers. It can be used in the laboratory for recording dust concentrations in animal experimentation, and for testing respirators and filters.

The function of this instrument should be sharply distinguished from that of smoke or blast-furnace dust recorders (2). Smoke recorders deal with dense clouds in smoke stacks. This instrument, on the other hand, deals with atmospheric pollution in industrial buildings, which, while usually greater than in general outside air, is far below smoke concentrations in stacks. Smoke recorders measure concentrations so dense that at their maximum they are opaque and totally shield a photo-sensitive cell from a light source in the opposite wall of the smoke stack. The instrument described here measures concentrations, which, at their greatest, would diminish a beam of light from a source a few feet distant by an amount measurable only with sensitive laboratory methods.

The relatively slight absorption of atmospheric dust, because of its scarcity, renders the smoke recorder method impracticable. Consequently, dust samplers present a two-fold problem: first, to concentrate the dust into conveniently measurable quantities; and second, to measure the concentrated dust. These two divisions, the sampling and the quantitation, exist in virtually all methods for dust determination. Unlike the present instrument, both are not ordinarily incorporated in a single piece of apparatus.

[1] Aside from giving a truer picture, a record showing "dust floods" may have unexpected hygienic significance. Cf. Mavrogordato, A.: "The Value of the Konimeter." Publications of the So. African Inst. for Med. Research, No. 17, p. 45, 1923. ". . . one is inclined to suspect [from animal experiments] that it is the intermittent exposure to relatively dense clouds that is the deciding factor in producing [silicosis]."

Of the five basically distinct methods of sampling, which have been used in dust determinators (3), the one adopted here is dry impingement. Dusty air passing through a slit at high velocity impinges the particles against a specially treated, moving, transparent film, thus forming a deposit of appreciable density. Quantitation is achieved by measuring continuously the changes in light transmitted through the deposit as the film progresses.

Dry impingement forms the basis of several instantaneous samplers, among which are the Owens jet counter (4), the Konimeter (5), and the Hill counter (6). In these, impingement of dust particles occurs on a glass surface, and their number is later counted microscopically.

The Owens automatic filter (7) operates in a concentration range equal to or lower than that for which our recorder was designed. In it, the dust is concentrated by automatically filtering known volumes of air through filter paper, leaving discolored spots on the white surface. These spots are quantitated visually by color comparison with standards. The instrument is not direct-reading, nor is it strictly continuous, since each observation, that is, each spot, represents an integrated sampling period of 15 minutes, or more. As McKay has pointed out (8), the dust measurements depend on the color of the dust itself.

Saylor (9) conceived a method for lessening the drudgery of counting Owens jet samples. Instead of viewing a fragment of the sample under the microscope, following the customary procedure, he photomicrographed the entire ribbon on a motion picture film, and counted the photographic images of the dust particles by causing them to interrupt a beam of light falling on a photo-cell connected to a magnetic counter, with suitable amplification.

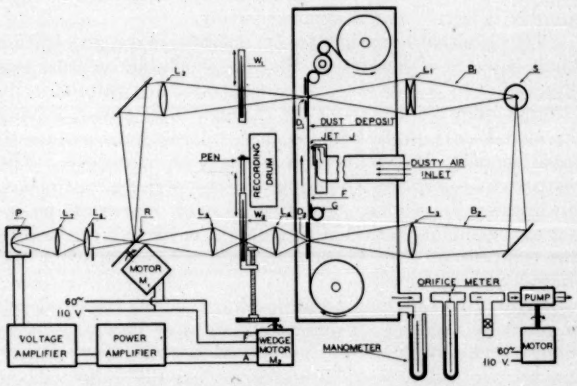
A brief outline of the present instrument will be given, followed by a more detailed description of the two main parts: the sampler, and the recording apparatus.

METHOD.

As shown in the schematic diagram, Fig. 1, dust in the incoming air is drawn at high velocity through a jet J and driven against the film F, which has been previously coated

with an adhesive at G. Two beams of light from the same source S are re-combined on a photo-cell P by a sectored mirror R, rotated at 60 cycles per second by a synchronous motor M_1. With clean air entering the sampler, both beams are of the same intensity, giving a steady illumination on the photo-cell, and there is no 60 cycle component in the photo-cell current. When, however, dust is being sampled, the deposit, moving upwards, diminishes the intensity of the beam B_1, causing a flicker, which in turn is translated into a 60 cycle alternating current by the photo-cell. The amplified

FIG. 1.



Schematic diagram of dust recorder. Heavy black rectangle represents air-tight box of the dust sampler.

signal is applied to the brushes of a motor M_2, whose field is connected to the same 60 cycle line that operates the synchronous motor M_1. By a threaded rod, the motor moves an optical wedge W_2 across the bottom beam in such a direction as to compensate for the reduction in intensity of the top beam due to the dust deposit. The wedge continues to move until the intensities of the two beams are restored to equality. Its position, as indicated on a chart by a pen connected mechanically to the wedge, is the measure of the density of the dust deposit. The armature of the wedge motor will turn in

a direction which depends on the phase relation of the field and armature currents. This relation, however, is directly controlled by the two beams of light: if the top beam is weaker than the bottom, the motor will revolve in one direction; if the top beam is brighter, that is, if the sampled air becomes cleaner, the motor will reverse. The density of the dust is in this manner measured in terms of the wedge by a self-balancing photo-electric system.

SAMPLER.

Jet and Film Investigations.

Owens (4) used in his jet counter a clean cover glass on which to catch dust particles by impingement. The application of this method to our continuous sampler with moving film instead of with glass was investigated. The efficiency of impingement, that is, the percentage of incoming dust retained on the film, was measured with test dusts set up in a 1600 cubic-foot chamber (10). The concentration of dust in the chamber was computed by titrating the weight of dust extracted by a laboratory electric precipitator (11) per unit air volume. The weight of dust impinged on the recorder film per unit air volume was measured also by titration. The ratio of the two would be unity, or the efficiency 100 per cent., if all dust stuck to the film. Three factors in particular were studied in an effort to construct a jet of high efficiency. They were: the jet-film separation, the jet width, and the air velocity through the jet. A fourth factor, the relative humidity of the dusty air, had no significant effect on the efficiency, although it was varied from about 30 to 100 per cent. For the sake of consistency, most of the samples were taken with a relative humidity 97 to 100 per cent. Three test dusts were used.

1. *Magnesium Oxide Fume.* This was generated by burning magnesium ribbon. Efficiencies up to 94 per cent. were obtained by correct choice of the three factors mentioned. These adjustments were critical.

Increasing the air velocity to 100–125 meters per second raised the efficiency to over 90 per cent., the other two factors being held constant at judiciously chosen values. Further increase in air velocity to over 300 meters per second resulted

in slightly decreasing efficiencies. The three factors, jet-film separation, jet width, and air velocity, were mutually dependent in that if one was altered, the other two had to be re-adjusted to regain a high efficiency. Sample settings, giving an efficiency of 92 per cent., will show the order of magnitude: jet-film separation, 0.05 cm.; jet width, 0.02 cm.; air velocity, 104 meters per second.

2. *Magnesium Oxide Powder.* This was obtained from a chemical supply house, and blown up in the chamber. The efficiencies were all below 30 per cent., and the jet adjustments were not critical.

3. *Calcium Carbonate.* This consisted of commercial whiting, blown up in the chamber. The efficiencies were all below 40 per cent., and the jet adjustments were not critical.

Immediately after being blown up, dusts 2 and 3 contained particles of considerably larger size than dust 1. However, as the recorder samples were taken after an interval of at least 1 hour, particles larger than 3 microns in diameter had fallen out. This calculation neglects flocculation. But as Brown and others (12) have demonstrated, flocculation makes such calculations unreliable. No change in efficiency was noted with age of cloud, even in clouds 18 hours old. The difference in efficiencies, therefore, cannot be definitely accounted for, although in comparing dusts 1 and 2, the difference in size would have at first appeared a reasonable explanation.

Whatever its cause, such a selective effect with different dusts could not be tolerated, although it should be realized that an efficiency of impingement which is less than 100 per cent. is quite permissible provided the efficiency is the same for particles of different size and chemical composition. A high efficiency has the practical advantage of making frequent cleaning of the apparatus unnecessary.

To raise the efficiency, transparent coatings were spread on the film to provide an adhesive surface. Among the substances used were: Canada balsam; gum acacia; diethylene glycol; gelatine moistened with water; mixtures of diethylene glycol or glycerine and a film solvent such as cellosolve, acetone, ethylene chloride, hot dimethyl phthalate, or dioxan; glycerine on clean film; glycerine on gelatine-coated film; and a mixture of equal parts of water and glycerine on gelatine-

coated film. The last of these preparations, wiped with a wick on a film previously coated with gelatine, proved the most effective; although other materials would also be satisfactory. The superiority of this combination lay in the following: the mixture did not discolor the film; it did not blow off nor dry when passing under the air jet; and it was absorbed by the gelatine after a few hours, leaving a dry permanent record. The film was not so moist that it soaked the particles and lessened appreciably their ability to scatter light.

With this adhesive, efficiencies for the three dusts were raised to over 90 per cent. They were not critically dependent on the jet-film separation (in the range 0.02 to 0.16 cm.), the jet width (in the range 0.009 to 0.030 cm.), nor the jet velocity (in the range 25 to 250 meters per second).

In practice, the particles are not uniform in size, nor even in shape and orientation, so that it is impossible to compute readily a calibration factor. The only accurate procedure is to calibrate the recorder in operation against a recognized dust sampler, as outlined later.

The calibration is valid only so long as certain characteristics of the dust, such as transmission factor, shape factor, effective cross-sectional area, and possibly electric charge, remain constant. However, contrary to one's first reactions, this limitation, inherent in the method, does not destroy the usefulness of the instrument. Air-borne particles in industrial atmospheres remain fairly constant in their chemical and physical properties from day to day. In fact, dusts generated by the same types of machines in different plants have virtually similar characteristics.

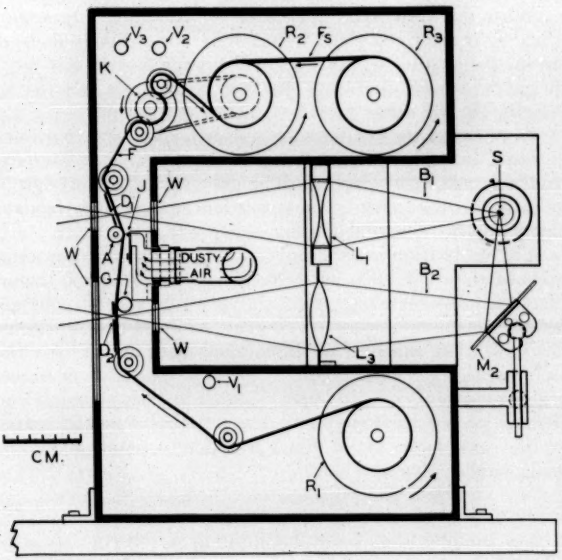
Construction of Sampler.

The sampler is shown in detail in Fig. 2. It consists of an air-tight metal box, having an inlet for dusty air to the jet J, and an outlet V_2 connected by tubing to an orifice meter, bleeder valve, and electrically-driven suction pump of 1 cubic-foot capacity. A third opening V_1 leads to a mercury manometer, which indicates a negative pressure in the box due to the resistance of the jet. Any blockage in the jet will be indicated by a rise in the manometer reading. The sampling rate may be varied at will, but a normal value is 25

liters per minute. The negative pressure in the box is of the order of 1 to 4 inches of mercury, depending on the width of the jet. Once adjusted, the air flow remains sufficiently constant for periods of considerable length.

The transparent film *F*, similar to 35 mm. motion-picture film base, is coated with gelatine before insertion and stored on the reel R_1. It moves upwards over rollers and a sprocket,

FIG. 2.

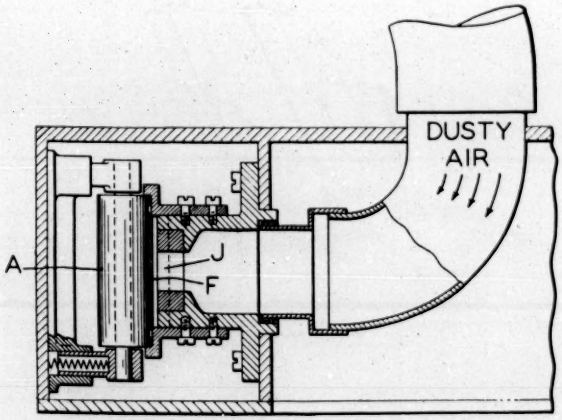


Vertical cross section of the sampler box. The dusty air enters from the back through an elbow.

and is coated with glycerine and water on passing over *G*, which consists of a cloth wiper wrapped around a finely perforated tube containing the glycerine-water mixture, and leading from a small reservoir on the back side of the box (see in Fig. 5). At *J* the film in a tacky condition picks up the fast moving dust particles, and carries them across a diaphragm

D_1, which, like D_2, is 0.45 cm. in diameter. Glass windows W permit two beams of light to pass through D_1 and D_2. A spring roller A holds the film at a fixed distance from the jet by pressing the film against two shoulders (Fig. 3). The jet itself is a slit, 1 cm. long and 0.02 cm. wide. Only the central part of the deposit passes in front of D_1, so that errors due to uneven edge deposits are avoided. The film is wound up on reel R_2 with its coils spaced from each other by F_s. The

FIG. 3.



Horizontal section of the jet J viewed from the top. As indicated, the dusty air intake is from the rear of the sampler box.

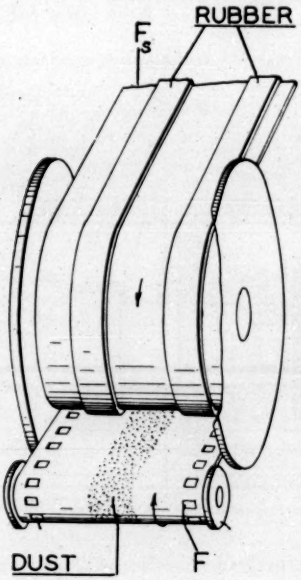
latter is a film of the same width as F, having narrow strips of rubber about 1 mm. thick cemented along its edge (Fig. 4). It prevents scratching of the dust, which would otherwise occur as the coils of F were wound on each other. It is useful only if the sample is to be preserved.

A dust particle on the center of the film requires 1.3 minutes to pass across D_1. There is, therefore, a slight integrating effect. This gives a smooth curve, should there be any irregularities in the mechanical drive of the film, as evidenced by faint striations across the dust band. In the present

model, there is a time lag of 4.5 minutes in recording due to the interval required for the movement of the dust from the jet to the diaphragm D_1.

An 1800 r.p.m. synchronous motor is geared as shown in Fig. 5 to drive the film and recorder chart at a speed of 20.4

FIG. 4.



Method of winding the dust-laden film *F* with a spacer film to prevent the dust deposit from being scratched.

cm. per hour, and the mirror *R*, which has alternate quadrants silvered, at 1800 r.p.m.

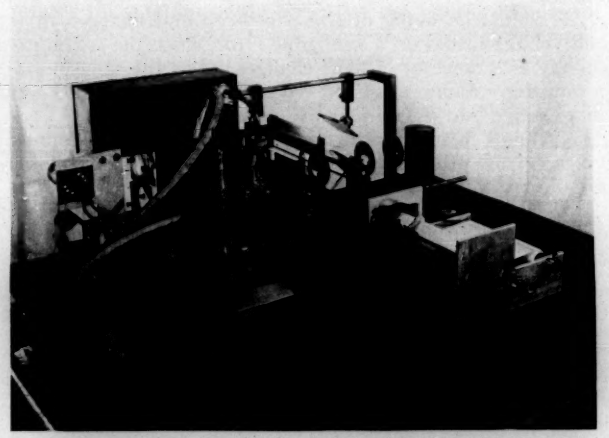
RECORDING APPARATUS.

Optical System.

The density of deposit on the film is used as a measure of the dust concentration in the air under examination. A null

method of densitometry is employed. The first of two beams of equal intensity (B_1, Fig. 1) taken from the same source travels through the deposit, while the second (B_2) travels through an optical wedge W_2. This wedge is the standard of measurement. It maintains the two beams at equal intensity by moving automatically in and out of beam B_2 to compensate for changes in beam B_1 due to the dust deposit.

FIG. 5.



Rear view of the sampler box, optical system, and recorder chart. The synchronous motor in the left foreground drives the film, the sectored mirror, and recorder paper. The 1-inch rubber tube above the motor is the dusty-air intake.

References to null methods of densitometry abound in the literature. In the majority, the relative strength of two beams is adjusted to equality (as detected by the eye or photo-sensitive cells) by manually controlled wedges or diaphragms. The outstanding example of automatic control is A. C. Hardy's color analyser (13), the photometric features of which are the same as in this dust recorder.[2]

[2] Professor Hardy made some helpful suggestions concerning the photoelectric recording mechanism.

A comparative or null method is essential in a machine of this type where it is unattended by a skilled operator for periods of several hours. With its use, the usual difficulty of keeping the various battery voltages and other circuit values constant vanishes. Chief among the advantages of the present recording apparatus are these.

1. Neither aging nor voltage fluctuations of the light source influence the reading, so long as the intensity does not fall to the point where added sensitivity in the amplifiers is needed.

2. Similarly, aging of the photo-cell and changes in the cell voltage introduce a negligible error, since the cell is used merely as a detector of light changes. For the same reason, a sensitive cæsium, gas-filled cell may be used instead of the more stable but less sensitive vacuum type.

3. Small changes in the amplifier plate, grid, and filament voltages, and other circuit constants, such as high resistances are of insignificant moment.

4. Even dirt, which might collect on the optical surfaces during long exposures to dirty atmospheres, is of small account, providing it collects everywhere at about the same rate. Actually, the chances of its doing so are favorable, since in one beam of light there are 20 surfaces, while in the other there are 21.

The details of the optical system are shown schematically in Fig. 1. The source S is a 100 watt, 110 volt photo-cell exciter lamp. It is normally operated on the direct-current line. On alternating current, a 120 cycle flicker is introduced, which, while it will not drive the wedge motor, taxes the amplifiers. Where no direct current line is available, the source may be a double-filament 32-candlepower lamp, with the filaments in parallel, and with the current supplied from a 6-volt storage battery.

The sectored mirror R, as already mentioned, recombines the two beams B_1 and B_2, so that they fall alternately on the photo-cell, one being cut out as the other is cut in. In accomplishing this satisfactorily, there is the practical difficulty of silvering and stripping the mirror so that the quadrants are bounded by sharp and true edges. Stray reflections from the edges, and spots on the silver coating are responsible for noises

in the amplifier which cannot be balanced out. Furthermore, the angular divergence of the two beams after leaving the mirror must be the same, for otherwise the images of the beams on the photo-cell cathode will not be exactly adjacent. First, they will overlap slightly, giving a bright line; and then, there will be a blank space, appearing as a dark line. These cause a flicker which cannot be balanced out. Extreme accuracy in mounting the mirror on its shaft is unnecessary, provided the reflected and transmitted beams spray over the edges of lens L_6. This expedient, plus the use of lens L_7, which determines the angular field of view of the photo-cell, assures that the two beams fall on the same spot on the photo-cell. Errors due to variations in sensitivity of the cathode are thus avoided.

The motor-driven optical wedge W_2 has an area of 2×15 cm., and a density range of 0–1.0. Its density increases linearly with its length.

Assuming the ideal conditions for which the absorption law holds, the setting of the recorder pen on the chart is therefore directly proportional to the dust concentration and air flow. It must be repeated, however, that these ideal conditions are never fulfilled in the field.

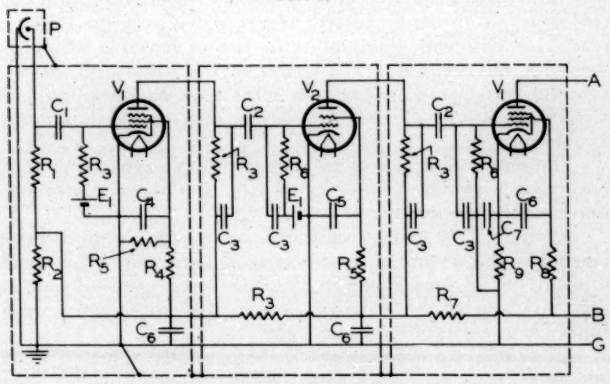
An auxiliary optical wedge W_1 is manually adjusted at the beginning of a run, with both beams passing through clear film areas, in order to obtain zero signal output when the recorder pen is at "zero" on the chart. By this simple procedure, which illustrates the advantages of a comparison method, dirt on the lenses or windows may be compensated for. Dirt, however, does not accumulate fast enough, even in exposed locations, to make adjustments of the zero point necessary more frequently than once a day. Test runs showed zero drift over twenty-four hours to be not more than 4 per cent., which, in dust measurements, is well within the desired accuracy.

Amplifiers.

The three-stage voltage amplifier circuit is shown in Fig. 6. It is built with individual stage shields on a metal base structurally separate from the power amplifier, shown in Fig. 7. The filament current for the voltage amplifier is derived from a storage battery, while that for the power unit is from

the alternating current line. Power for all the plate circuits is rectified by one type 83 mercury-vapor rectifier, and filtered with large capacities and chokes. The power output tubes are arranged as in Class B amplifiers. Their plate impedance is matched to the armature of the wedge motor, the impedance of which is 126 ohms. About 9 watts are required to start

FIG. 6.



Circuit diagram of voltage amplifier.

C_1— .003 uf.	R_1—20 meg.	R_8—.25 meg.
C_2— .005 uf.	R_2— 2 meg.	R_9—3000 ohms.
C_3— .0025 uf.	R_3— 1 meg.	P —Photo-cell.
C_4— .1 uf.	R_4—10 meg.	E_1—1.5 volts.
C_5— .25 uf.	R_5— 5 meg.	V_1—Type 38.
C_6— 1.0 uf.	R_6— .5 meg.	V_2—Type 36.
C_7—25.0 uf.	R_7— .4 meg.	

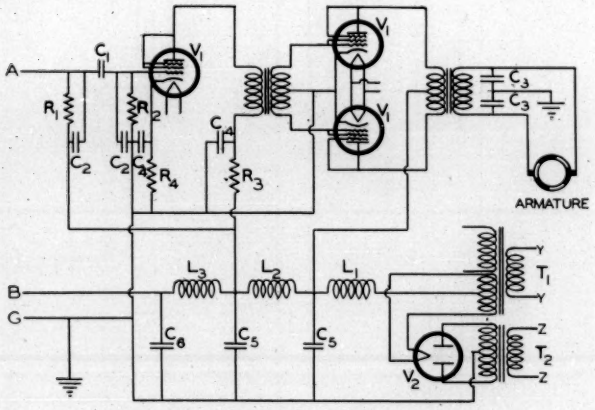
the motor turning. Chattering of the armature is prevented by shunting it with two 0.01 uf. condensers in series, with their junction grounded. The amplifiers and other metal parts are thoroughly grounded. Since the density variations in the dust deposit are fairly gradual—a matter of several minutes—the wedge motor seldom turns at top speed, and there is no occasion for "overshooting."

Safety devices prevent the wedge from moving beyond its range. If the dense end is being driven into the light beam B_2 with the likelihood of the pen running off scale, an opaque border at the dense end of wedge will generally cause the wedge

to "hunt" between the totally opaque region and the adjoining dense but slightly transparent area. To arrest movement off scale in the opposite direction, a contact (Fig. 8) operates a relay opening the motor field and lighting a warning signal.

The gain of the voltage amplifier is 90 DB as measured at 60 cycles per second.

FIG. 7.



Circuit diagram of Class B power amplifier.

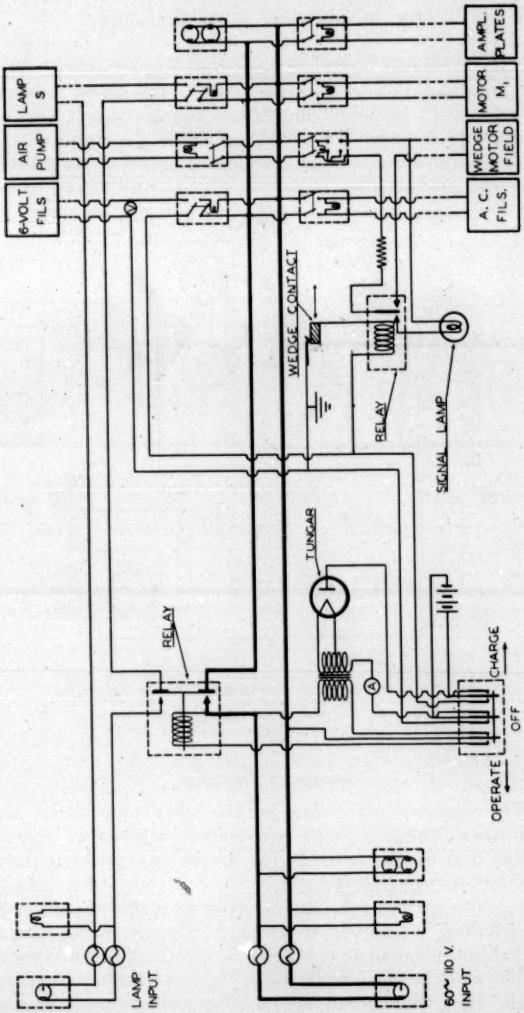
C_1— .1 uf.	R_1—40,000 ohms.	L_1—Swinging choke.
C_2— .03 uf.	R_2—30,000 ohms.	L_2—Smoothing choke.
C_3— .01 uf.	R_3— 8000 ohms.	L_3—Smoothing choke.
C_4— 8.0 uf.	R_4— 1100 ohms.	T_1—Fil. trans.
C_5—16.0 uf.	V_1—Type 59.	T_2—Plate trans.
C_6— 8.0 uf.	V_2—Type 83.	

ASSEMBLED RECORDER.

The various components of the laboratory model have been assembled on a truck, shown in Figs. 8 and 9. On top are the dust sampler and optical system protected from stray light and dirt by a box cover. The dust inlet tube is in the rear. Also in the rear, and projecting outside the cover for accessibility, is the recorder chart. On the shelf beneath are the amplifiers, storage battery, Tungar rectifier, and pump.

The truck is wired, as shown in Fig. 8, with a master switch, which, when thrown to one side, places all the recorder units

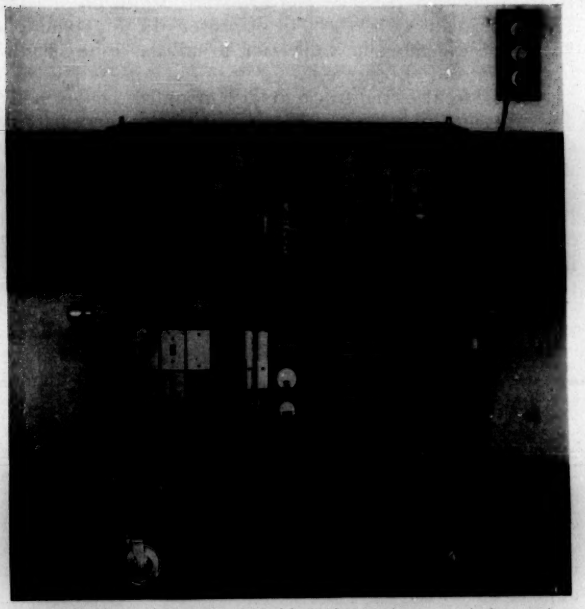
FIG. 8.



Wiring diagram of assembled recorder. The wedge contact is located on the carriage of the optical wedge W_1, and operates a signal lamp indicating trouble with the balancing mechanism.

in operation; when in the middle, disconnects them all; and when thrown to the other side, puts the storage battery on charge. For facility of adjustment in this experimental model, each electrical unit is separately controllable. Power

FIG. 9.



Front view of assembled recorder. At the left end of the panel are receptacles for power input from the line; in the middle are the flowmeter and pressure manometers, air-flow valve, master switch, and meters; and at the right are seven switches and pilot lamps for individually controlling the elements of the mechanism. The cables at the right lead to the three signal lamps shown above the apparatus. Within the box-shaped cover may be seen, at the left, a cylindrical shield containing the photo-cell; in the middle, motor M_2 and gears which drive the wedge W_2 in and out; at the right, the U-shaped dust sampler; and at the extreme right the lamp S.

is led into the recorder through the two polarized receptacles at the left in Figs. 8 and 9. The bottom one is the 110 volt alternating current feed; while the top is for the lamp current, which may be derived from the line or from a storage

battery. Seven switches on the right control the individual circuits, and are represented by dashed rectangles in Fig. 8. All circuits are connected with pilot lamps. The switches are double-pole, single-throw toggle switches. A four-way switch is connected as a reversing switch in the leads to the field of the wedge motor. The purpose of this is to correct the phase relation between the field and armature, which on starting the apparatus may be 180° out of phase. In this condition, the wedge will move in a direction to unbalance further the system, instead of balance it.

On the front of the truck are also mounted the flowmeter and pressure manometers, battery voltmeter, and battery charging ammeter. A signal lamp, at the right side, lights up if the optical wedge W_2 should move off scale at its thin end. Three indicator lamps (not shown in Fig. 8) operated by suitable contacts enable one to tell at a glance the position of the wedge W_2 and the recorder pen. In an industrial installation auxiliary exhaust fans could be controlled by these circuits.

CALIBRATION.

The dust recorder is calibrated in the following manner against the Greenburg-Smith impinger, which is the standard instrument for dust estimation in this country.

An artificial dust cloud in a gas-tight chamber, or the dusty air of a factory may be used, although the latter is desirable if the recorder is to be used in that plant. The recorder is set in operation. At intervals impinger samples are taken and counted, and the resulting dust concentrations are correlated with the corresponding excursions of the recorder pen. In this way the chart divisions may be calibrated to read directly in units of dustiness.

Preliminary calibrations have been made in the laboratory against silica blown up in a dust chamber. The impinger counts were made with dark-field illumination, and these were converted to light-field counts by an empirical ratio depending on the age of the cloud (14). The approximate sensitivity of the instrument judged by these tests is: one chart division (0.55 cm.) = 5×10^6 particles per cubic foot of air. (The chart contains 24 divisions.)

The range of dustiness recorded by the instrument may be increased or decreased by using a denser or less dense wedge, respectively, in the position W_2, Fig. 1.

CONCLUSION.

It should be emphasized that the method employed differentiates in no way between particle size and number.[3] The basis of the instrument, the diminution of light transmitted through a dust layer, is concerned with the combined, not the separate, effect of size and number. Other chemical and physical properties of the dust as well will affect the record in an indiscernible manner. The machine therefore, is limited to a given industry, or else the chart must be interpreted with various scales corresponding to the dust being examined. With an acceptance of these limitations, however, the machine presents some distinctly novel advantages over existing instruments: a permanent sample, a graph that can be read with facility by any unskilled observer, and a continuous record of rapid dust fluctuations over a period of many hours.

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[3] The unit of dustiness used in dust codes and specifications is millions of particles per cubic foot of air. No recognition is thus given the question of size, which of course, is fully as important as number in defining a particular dust.

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PETROLEUM REFINING BY MEANS OF SELECTIVE SOLVENTS.*

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INTRODUCTION.

The first oil well ever drilled was completed in August 1859 by Colonel Drake on an island in Oil Creek, Pennsylvania. Although it is safe to say that it contained lubricating oil, it apparently contained more lamp oil, for J. J. McLaurin in his "Sketches in Crude-Oil" (1898) says:

"Cheap and abundant light the island-well on Oil-Creek assured the nations sitting in darkness. If there are 'tongues in trees' and 'sermons in stones' the trickling stream of greenish liquid murmured: 'Bring on your lamps—we can fill them!' The *second* oil-well in Pennsylvania, eighteen miles from Col. Drake's, changed the strain to: 'Bring on your wheels—we can grease them!'"

Then, describing the "bringing in" of this second (French Creek) well, also in 1859:

". . . Two men plied the pump vigorously. A stream of dark-green fluid gushed forth at the rate of twenty-five barrels a day. It was heavy oil, . . . free from grit and smooth as silk. The greatest lubricant on earth had been unearthed."

Millions of dollars are spent annually in reiterating the last statement—and justifiably. Since 1859 hundreds of thousands of wells have been completed in hundreds of localities throughout the world, and the vast majority of the crudes contained lubricating oils. If from each of these crudes lubricating oil had been recovered by standard methods, they would have covered a very wide range of quality, yet none of them would have been appreciably superior to that from the

* Presented at a meeting held Thursday, December 14, 1933.

earliest member of the far-famed group of Pennsylvania Crude Oils.

Nature, then, although supposedly engaged in the manufacture of lubricants for the last hundred million years, has never improved upon Pennsylvania. Natural crudes do contain some components better than Pennsylvania, but always they are blended with components of far poorer quality.

Selective solvents have offered a means of taking apart the tremendously complex mixtures of good and bad represented by crudes, so that it is possible, not only to produce oils of Pennsylvania quality from crudes of inferior grade, but also to separate *better-than-Pennsylvania* oil from almost any crude, including Pennsylvania itself.

COMPOSITION OF PETROLEUM AND MANUFACTURE OF LUBRICATING OILS.

As has already been indicated, the complexity of the composition of petroleum is, to one whose scientific pursuits would seem to demand that he understand it, little short of terrifying.

In the first place, the hundreds, or possibly thousands of compounds which go to make up a crude petroleum vary in boiling point from those which boil below normal temperatures and are therefore present as dissolved gases, to those whose boiling points cannot be determined, although they are surely above 1000° F. Furthermore, the string of compounds is practically unbroken; there are present those which boil at or near any point between the two extremes given.

Differences in boiling points formed the basis of the first means of separation of crude petroleum into fractions of different properties, namely distillation, and this process is still by all odds the most important and widely used.

If a crude oil be charged to a still, and heat applied, the lowest-boiling constituents will of course be vaporized, after which they may be recondensed and collected as a liquid. These will be followed by constituents of higher and higher boiling points, and it is obvious that, during the course of the distillation, the distillate may be divided into as many fractions as desired, each of which will be different from all the others. If, however, the still be heated much above 700° F., the compounds remaining (all of which have very high boiling

points) will, in part, be broken down into compounds of lower boiling point. This is, of course, the foundation of the tremendously important process of cracking, by means of which the refiner is enabled to produce from the average crude at least twice as much gasoline as was originally put there by nature. When, however, it is desired to recover the high-boiling constituents without decomposition, the boiling points are lowered by conducting the distillation (during the latter stages) under high vacuum, or by the introduction of steam into the still, which, to use a common expression, "carries over" the compounds which would not, at that temperature, "go over" by themselves.

Even by the use of vacuum or steam, or steam and vacuum together, there will remain in the still material of excessively high boiling point, which, for convenience, we may term asphalt.

In general, crudes are split by distillation into fractions somewhat as follows:

Fraction.	Approximate Boiling Range, ° F.	Source of:
1	95–375	Gasoline, special naphthas, etc.
2	350–500	Lamp oils
3	490–550	Heavy burning oils; gasoline by cracking.
4	530–850	Light lubricating oils; wax if present.
5	840–1000+	Heavy lubricating oils. Wax is frequently present but seldom recovered as such.
6	1000 and higher	Asphalt.

Gasoline may be produced, by cracking, from any of the cuts which are heavier than gasoline, i.e., 2–6; indeed the entire crude may be charged to a cracking plant which not only separates the gasoline occurring in the crude, but also transforms much of the remainder into gasoline.

In producing lubricating oil, however, it is necessary to remove fractions 1–3 inclusive. Cuts 4, 5 and 6 each contain lubricating oil, and may be further processed singly or in any desired combination.

First of all the lubricant should be liquid at temperature of use, which is to say that wax should be absent. In most

instances, therefore, it is necessary to remove wax. The processes by which this may be accomplished are many and interesting, but cannot be discussed here. As for the other refining methods which have been in vogue for generations—and still are—their prime purpose, it must be admitted, has been to improve the appearance of the oil. A good lubricating oil, or, perhaps more accurately a lubricating oil which will look good to the public, should vary in color, by transmitted light, from yellow to deep red; furthermore, its cast by reflected light should be green.

These ends have been accomplished, principally, by two means:

1. Application to the oil of chemicals, usually sulfuric acid, which react with the highly colored bodies and form a heavy sludge which can be removed.
2. Application to the oil of adsorbent earths, such as fuller's earth, which preferentially adsorb the highly colored bodies.

To be sure, such processes, particularly the first, remove the most reactive, and hence the least stable, compounds, so that improvement in general stability of the oil always results, but the success of the treatment has been judged, in the main, by the color of the finished product.

If the crude is originally free of wax, and if the distillation is carried out with extreme care—say under vacuum—much of the treatment just discussed may be omitted.

DIFFERENCES IN LUBRICATING OILS.

While, from almost any crude, there may be produced, by means of the methods discussed, lubricating oils which look alike, the similarity ceases abruptly at that point; their physical properties vary widely, as a result of variations in chemical composition. It will be necessary, then, to make brief reference to the chemical constitution of lubricating oils.

It should be stated at the outset, however, that woefully little is actually and definitely known of the composition of lubricating oils; it is possibly only to generalize by analogy from those fortunately simpler fractions—such as gasoline—whose composition is fairly well known.

With the exception of very minor quantities of sulfur, oxygen, nitrogen and a few others, petroleum is made up of but two elements, namely, carbon and hydrogen. The compounds (hydrocarbons) resulting from the combination of these elements vary from methane, containing but one carbon atom, to those containing perhaps two-score carbon atoms and about twice as many hydrogen atoms. The number of different ways in which such a large number of atoms may be linked together (and each different type of linkage produces a distinct compound) defies calculation, and it also accounts for the bewilderingly complicated makeup of crude oils, and for the well-nigh insuperable obstacles confronting him who would isolate and identify the chemical individuals.

The almost numberless compounds can, however, be divided into two classes; first those in which the carbon atoms are connected in chains, either straight or branched, and second those in which the carbon atoms form closed rings. There are, of course, intermediate compounds which combine the two types of structure; that is, a chain may be attached to a ring.

That class of lubricating oils believed to be composed predominantly of *chain* compounds is termed *paraffinic*, and is exemplified by Pennsylvania oils. The opposite type of oil, consisting principally of *ring* compounds, is frequently found in crudes of Gulf Coast origin, and is termed *naphthenic*. Most oils, quite naturally, fall between the extremes just mentioned.

The types of oil are recognized by their physical characteristics. The property common to all lubricating oils is that of viscosity. It may be defined as the resistance offered by a fluid to the relative motion of its particles. The measure of viscosity most widely used in this country is that obtained by means of the Saybolt Universal viscosimeter. It expresses, in seconds, the time required for 60 cubic centimeters of oil, at a definite temperature and contained in a vessel of specified dimensions, to run through an orifice, of specified size, placed in the bottom of the vessel. The more viscous oils will of course require the greater time.

The viscosity of all oils decreases as the temperature is raised, so that a viscosity without a stated temperature is

meaningless. Thus an oil may be of 100″ viscosity at 210° F., but of 3000″ viscosity at 100° F.

Viscosity is the most convenient basis upon which to compare the properties of lubricating oils of different type. If a highly paraffinic (Pennsylvania) oil, of, say 100″ viscosity at 210° F., were compared to a highly naphthenic (Gulf Coast) oil of the same viscosity at 210° F., their other properties would be found to be as follows:

	Paraffinic (Pennsylvania) (Chain Structure).	Naphthenic (Gulf Coast) (Ring Structure).
Specific Gravity	low	high
Boiling Point	high	low
Molecular Weight	high	low
Rate of change of viscosity with change of temperature	low	high

The last property named—the rate of change of viscosity with change of temperature—is by all odds the most important, particularly because it may immediately be interpreted in terms of service in the average motor car.

In order that the engine may be properly lubricated while running, viscosity must be reasonably high at high temperatures. With all oils, as the temperature drops the viscosity increases, and every motorist is familiar with the difficulty of starting a car in cold weather. This difficulty is, of course, due to the high viscosity of the cold oil. Let us say that, with the Pennsylvania oil referred to above (100″ viscosity at 210° F.), used to lubricate a certain car, the battery is *just able* to start the engine at 0° F. If the Pennsylvania oil were removed, and replaced by an oil of extreme Gulf Coast type of the same viscosity at 210° F., the battery would be quite unable to start the engine at 0° F.; indeed it could not start it until the temperature of the oil had been raised to about 50° F.

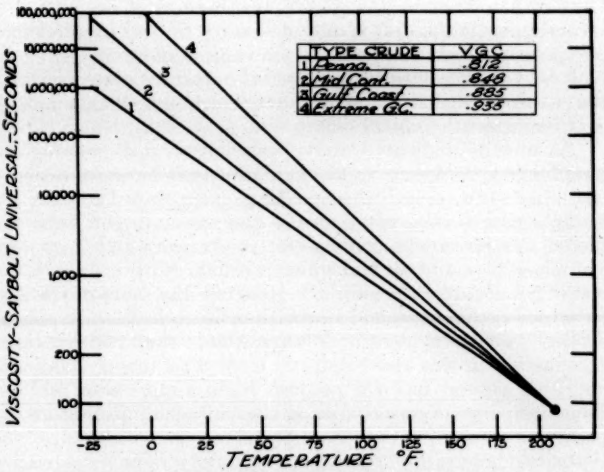
This is expressed in terms of viscosity in Fig. 1.

While all the oils shown are of the same (100 seconds) viscosity at 210° F., the viscosities at 0° F. vary from about 100,000″ for the Pennsylvania to about 100,000,000″ in the case of the Extreme Gulf Coastal. In other words, at the boiling point of water, the Gulf Coast Oil would flow through a given orifice, under the same conditions of pressure, etc., as

rapidly as the Pennsylvania, but at 0° F. the Coastal would take one thousand times as long.

Returning to the matter of starting an engine—Fig. 1 shows that the Pennsylvania oil is of about 100,000″ viscosity at 0° F., while the Extreme Coastal is of that same viscosity at 50° F., hence the resistance to starting would be about as great at 50° F. with the second oil as at 0° F. with the first oil.

FIG. 1.



Range of viscosity-temperature slopes for natural oils.

QUANTITATIVE EXPRESSION OF TYPE.

It was stated above that oils of the Pennsylvania type are referred to as *paraffinic* and those of the Coastal type as *naphthenic*. There have been developed several methods for qualitatively expressing the differences displayed by oils; that is the various degrees of paraffinicity. The methods depend upon expressions involving, for each oil, either viscosity values at two temperatures, or a single viscosity and the specific gravity.

Qualitatively, the results obtained by the two lines of attack agree. The author has found, however, as have others within his knowledge, that figures depending upon one viscosity and the gravity are not only easier to determine, but may also be more accurately determined. Furthermore, they seem more suitable for the purpose of studying a mass of experimental results.

For the sake of simplicity, therefore, but one measure of paraffinicity will be used in this paper, namely the Viscosity-Gravity-Constant (V. G. C.).[1] Its method of derivation is inconsequential here; it is only necessary to bear in mind that *paraffinic* oils exhibit *low* V. G. C. values, and *naphthenic* oils *high* V. G. C. values. Among the naturally occurring oils, the values range from about .810 for Pennsylvania oils to .935 for extreme Coastal oils.

As already indicated above, distillation does not change paraffinicity, and the effect of acid or clay is but minor, hence the refiner has, practically speaking, been forced to take for his lubricating oils, what nature happened to put into the crude. To be sure he could select good crudes, but they were of limited production, and quite possibly did not fit into the rest of his picture, for while the good old dinosaurs of the Appalachians may have laid down their lives in the interest of proper twentieth century lubrication, the Pennsylvania gasoline which was also produced from their mighty bodies is far from a good fuel for modern high compression motors. That users have long recognized the differences in motor oils, whether or not they expressed them in terms of V. G. C. or viscosity-temperature coefficient, is amply demonstrated by the sizable premium which has long been, and is still being, paid for Pennsylvania oils.

DEFINITION OF SELECTIVE SOLVENTS.

Lubricating oil is a complex mixture of organic compounds —hydrocarbons—and it has been pointed out that their number is legion. There are known many thousands of liquid organic compounds, many of which contain atoms others than carbon and hydrogen. There is a relatively smaller number of liquid inorganic compounds. For the present

[1] Hill and Coats, *Ind. and Eng. Chem.*, **20**, 641 (1928).

purpose all of these may be divided into three classes as follows:

1. Those which are completely miscible with lubricating oil at any normal [2] temperature. If diethyl ether, carbon tetrachloride or carbon disulfide be added to lubricating oil, they will mix completely with the oil. Compounds of this class may be said to have extremely high solvent power for oil.

2. Those which are substantially immiscible with oil; that is have little or no solvent power for oil. Water, methyl alcohol and glycerine are examples of this class.

3. Those which, at some reasonable [2] temperature, are *partially* miscible with oil; that is part of the oil is dissolved in the solvent, but part remains undissolved. Examples are nitrobenzene, phenol, aniline and acetone. These are *selective solvents*.

The matter of temperature is an extremely important one. For example, a mixture of aniline and oil can readily be heated to such a temperature that all the oil is dissolved in the aniline, and at that temperature aniline acts like members of the first class. If it be cooled, however, some of the oil is thrown out of solution, and at that temperature aniline is a member of the third class. With carbon tetrachloride, on the other hand, all the oil remains in solution at any reasonable temperature.

The same classification can be stated in another, and perhaps more significant manner (always assuming "reasonable temperatures"):

1. Compounds which form one homogeneous phase with oil.
2. Compounds which form two phases with oil, but with substantially all the oil in one phase and none in the other.
3. Compounds which form two phases with oil, with substantial amounts of oil in each phase. (Selective solvents.)

In selective extraction of lubricating oils, then, it is always necessary to have two phases, that is, two liquid layers. One

[2] This may be only roughly and arbitrarily defined, in terms of practical operation. Let us say that it is not feasible to use temperatures above 400° F., or below − 20° F.

of these contains most of the solvent, with part of the oil (extract) dissolved therein; the other is principally undissolved oil (raffinate), with some solvent dissolved in the oil. Common terminology is (as indicated parenthetically above) the *extract* layer and the *raffinate* layer, respectively.

To complete the extraction, the two layers are separated, and solvent is removed from each, usually by distillation. The two oil fractions are then known as *extract* and *raffinate*, respectively.

HISTORY OF SOLVENT EXTRACTION.

Before proceeding to a consideration of the details of solvent extraction, and the results attained thereby, it might be well to digress for a moment to take brief notice of its historical development.

Back in the days when refiners were using their ingenuity to put as much gasoline into kerosene as the law would allow, and wishing they could throw the rest of the gasoline into the sewer or river, the burning quality of kerosene was an all important matter. Octane rating had never been heard of, and the viscosity-temperature coefficient of lubricating oils was unimportant because there was plenty of Pennsylvania crude to supply all the demands for lubricating oils. Lazar Edeleanu found that if he brought kerosene into contact with liquid sulfur dioxide, certain constituents were dissolved, and the remainder (the raffinate), when freed of sulfur dioxide, burned more satisfactorily than did the material before extraction.

That was about twenty-five years ago, and probably represented the first application of selective solvents to petroleum products.

Subsequently other solvents were applied to various fractions of petroleum. The purpose was usually the removal of some relatively small amount of material. For example, gums or resins could be extracted from gasoline. Then it was found that if a small amount of material were thus removed from crude lubricating distillates, the raffinate could more easily be acid treated to the desired color, and with the destruction of less oil.

Presently it began to be realized that the *extract* from such

treatments was always naphthenic, and that the raffinate was accordingly more paraffinic, that is, more like Pennsylvania. Nevertheless, it is only very recently that it has finally been demonstrated that, by the removal of substantial instead of insignificant amounts from a Coastal or naphthenic type oil, there may be obtained as a raffinate an oil of Pennsylvania quality, or better. Even Pennsylvania has been made to yield up its naphthenic constituents—which it was long supposed not to contain—and has itself been improved in quality.

In other words, Nature did not produce one kind of oil from plesiosaurs and another from pterodactyls, but all sorts of oil from whatever came to hand, varying only the proportions of the various types.

REQUIREMENTS FOR A SELECTIVE SOLVENT.

From the standpoint of the refiner, the problem is to recover, from a given lubricating fraction, the greatest possible yield of the high quality oil at the minimum cost. The process involves mixing solvent and oil; separating the resulting two layers, and recovering the solvent from each layer. The qualities of a satisfactory solvent may therefore be stated as follows:

1. Non-reactive with the oil under the conditions of the process.
2. Capable of effecting a sharp separation between paraffinic and naphthenic constituents.
3. Of such solvent power that a given separation may be effected by the use of reasonably small amounts of solvent.
4. Easily and completely separable from the respective fractions, preferably by distillation.

Many otherwise interesting solvents must, of course, be removed from consideration on the basis of No. 1 or No. 4 above. Reaction would be destructive of both solvent and oil (the solvent is usually many times as expensive as oil) and the losses would be prohibitively expensive. If the boiling point of the solvent be as high, or nearly as high as some of the oil constituents, separation by distillation is manifestly impossible.

All the solvents discussed below are satisfactory from these standpoints, and what follows, therefore, will concern items No. 2 and No. 3. They are closely inter-related. It is obviously desirable to obtain the highest possible yield of the desired quality, but the major cost of the extraction is represented by the fuel costs for redistillation of solvent, and by the cost of the small percentage of the solvent which is lost in each operation. Both of these costs increase as the amount of solvent employed increases. It may well be found advisable, from a cost standpoint, to accept a yield somewhat lower than the maximum attainable, if by so doing the amount of solvent used in the process may be radically decreased.

COMPARISON OF EFFICIENCY OF SOLVENTS.

To illustrate the differences among solvents, five representative ones have been chosen from a much larger group which has been tested. Results with many of these solvents were reported in detail in a previous publication.[3] The lubricating stock to which the solvents were applied was of the following characteristics:

Saybolt viscosity at 100° F., seconds	612
Saybolt viscosity at 210° F., seconds	57
Specific gravity at 60° F.	0.930
Gravity, degrees A. P. I.	20.6
Viscosity-gravity constant (V. G. C.)	0.874

It will be noted that the stock is of Coastal (naphthenic) type. The task set for each solvent is to produce therefrom oil of Pennsylvania (paraffinic) characteristics.

Figure 2 presents the results purely on a basis of the efficiency of separation between paraffinic and naphthenic constituents, regardless of the amount of solvent necessary to effect the separation. The vertical line at V. G. C. = 0.874 represents the stock; points to the left represent raffinates and those to the right extracts. The "Per Cent. Raffinate" and "Per Cent. Extract" scales run in opposite directions, so that the two points resulting from a single extraction lie, within experimental accuracy, on the same horizontal line. For

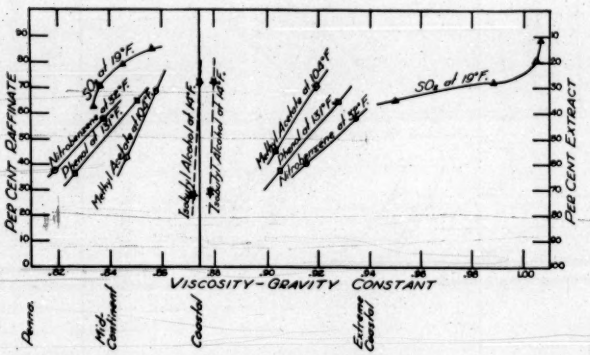
[3] Ferris, Birkhimer and Henderson, *Ind. Eng. Chem.*, **23**, 753 (1931).

example, one of the treatments with liquid sulfur dioxide (SO_2) resulted in an 80 per cent. raffinate of 0.845 V. G. C. and a 20 per cent. extract of 1.05 V. G. C.

Each pair of points represents an individual extraction in which the stock was extracted with fresh solvent. These are known as "single batch" or "batch" extractions. Other methods of extraction will be discussed below.

On the basis of Fig. 2, sulfur dioxide stands out as the *most selective* of the five. It separates from the stock extremely naphthenic materials (points at extreme right); and it

FIG. 2.



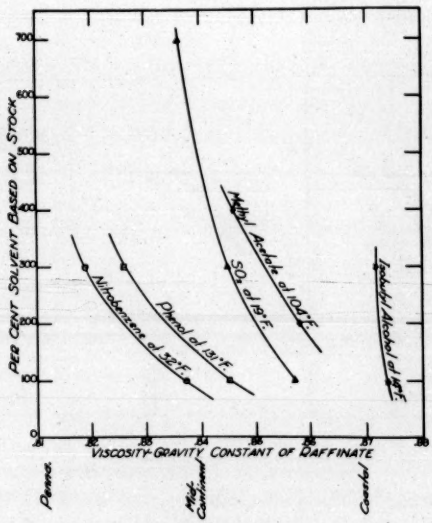
Comparison of selective solvents.
a. Efficiency of separation.

produces the highest yields of material of .840 V. G. C. (Mid-Continent grade). The manner in which the raffinate curve (at the left) slopes sharply downward, however, would tend to indicate that sulfur dioxide is incapable of producing, from this stock, oil of better than .830 V. G. C. Nitrobenzene and phenol, however, show no indication of having reached their limits; .810–.815 V. G. C. seem well within reach.

Isobutyl alcohol is a selective solvent by courtesy alone, for while it separates the oil into two fractions, they are so similar, at least as indicated by V. G. C., that the labor of separation has indeed been lost.

It was remarked that Fig. 2 takes no notice of the amount of solvent required. When this item is considered (Fig. 3), quite a different light is thrown on the matter. (In this and following figures, only the raffinate points are shown. Extract points would of course be at the right as in Fig. 2). To produce the larger yield of .840 V. G. C. some 600 volumes of sulfur dioxide per 100 volumes of stock are required, whereas

FIG. 3.

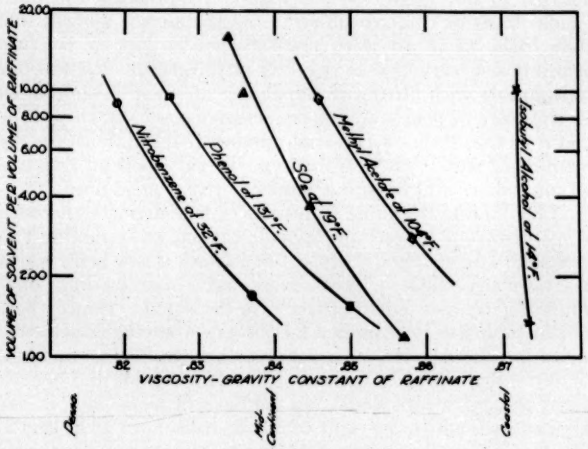


Comparison of selective solvents.
b. Volume efficiency.

considerably less than 100 volumes of nitrobenzene are necessary. On the other hand 200 per cent. by volume of nitrobenzene will result in a quality which would seem to be impossible for sulfur dioxide.

Figure 2 has emphasized efficiency of separation; Fig. 3 volume efficiency of the solvent; in Fig. 4 these are combined

FIG. 4.



Comparison of selective solvents.
c. Over-all efficiency.

to show the volume of solvent required to produce one volume of raffinate of definite quality.

As indicated above, upon these relationships, more than any other, rests the size of the plant and the amount of solvent which must be handled, hence they may justly be considered highly important. The following values, taken from Fig. 4, may serve to emphasize the differences between these solvents:

Solvent.	Volume* of Solvent Required to Produce One Volume of Raffinate of V.G.C. of:		
	0.860.	0.840.	0.820.
Nitrobenzene	0.5	1.4	8
Phenol	0.9	3.0	18
Sulfur dioxide	0.9	6.5	Impossible
Methyl acetate	2.3	21	Impossible
Isobutyl alcohol	Impossible	Impossible	Impossible

* By batch extraction.

Hundreds of prospective selective solvents have been examined in our laboratories. Figure 4 represents the most logical basis of comparison so far as the author knows. On that basis, there are very few solvents as poor as isobutyl alcohol, and very few as good as nitrobenzene. Of the few comparable with nitrobenzene, almost all must be eliminated on the score of poor stability or excessive cost. If, then, it be taken as the author's personal opinion (backed, however, by reams of data) that nitrobenzene is an excellent selective solvent, there still remain a number of very good ones.

The Atlantic Refining Company is demonstrating its faith in nitrobenzene by erecting a plant capable of extracting two thousand barrels of oil daily. But in such a new field, which has been investigated by many research organizations, unanimity of opinion could scarcely be expected. Hence there are, or soon will be, commercial plants employing as selective solvents phenol, its near-relative cresylic acid, furfural, dichlor ethyl ether, and mixtures of sulfur dioxide and benzol. All of these solvents would, on the basis of tests made in our laboratories, fall to the right of nitrobenzene on Fig. 4; that is larger volumes of solvent would be required to produce a given volume of raffinate of definite quality. Furthermore, some of the solvents are incapable of producing as high a degree of paraffinicity as is obtainable with nitrobenzene.

That the remainder of the discussion will be confined to nitrobenzene is, happily, only secondarily attributable to the personal beliefs, just expressed, of the author. The primary reason, scarcely open to objection, is that data of the type which follow, but obtained with the solvents just mentioned, are for the most part unavailable to the author.

A change in nomenclature must be noted before proceeding. Nitrobenzene raffinates are referred to as "nitraffins" and the extracts as "nitrenes." The derivation of the terms is apparent from NITRobenzene, parAFFIN and naphthENE, a nitraffin being a paraffinic fraction obtained by nitrobenzene extraction.

VARIOUS TYPES OF EXTRACTION PROCEDURE.

The results presented above were obtained by single batch extractions, as explained. There are at least three other

methods of carrying out the extractions, each of which is more efficient than batch. It should be stated, however, that the efficiency of any solvent which we have investigated is increased, by such methods, approximately in the same proportion. In other words, comparing solvents by extraction methods other than batch would not substantially alter the results with respect to efficiency from those presented above. The other methods are:

1. Multiple Extraction: The raffinate from the first extraction is again treated with fresh solvent, etc.

2. Batch Counter-current: Several treaters are employed, separations being effected in each, with the raffinate and extract layers being transferred—in opposite directions—from one treater to another. In effect, each batch of solvent is used as many times as there are treaters in the system; initially, upon raffinate about to be removed; finally, upon incoming stock.

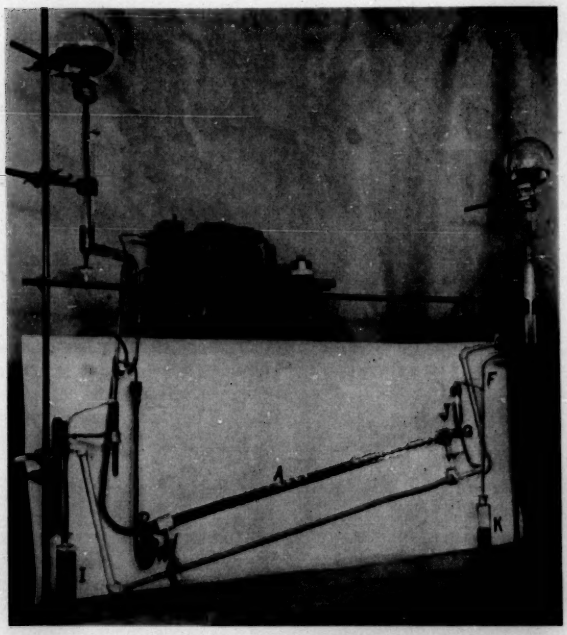
3. Continuous Counter-current: Solvent and stock pass counter-current through a tube or tower treater, being agitated during passage. Settling chambers are provided at each end to allow the 'phases to separate. With a tube of any considerable length, this type of treatment is equivalent to a very large number of stages; in fact, since the composition of both the extract phase and the raffinate phase at any point in the tower differs from the composition at any other point, it may be considered to be a method by which the solvent is employed an infinite number of times before being withdrawn from the system.

A laboratory continuous counter-current extractor is shown on Plate I.

The extraction is carried out in the inclined tube *A*. The untreated oil in flask *B* enters the system at a constant rate at *C*, and the tube at *D*, while the solvent (nitrobenzene) in flask *E* flows into the system at *F* and the tube at *G*. Due to its greater specific gravity the nitrobenzene flows down the tube, while the oil flows up. Contained in the tube is a bladed agitator driven by the motor through a flexible shaft. This agitator brings the descending nitrobenzene into intimate contact with the ascending oil, and the naphthenic constituents are dissolved in the nitrobenzene. The nitrene solution

flows into the chamber *H*, where entrained oil is allowed to rise and re-enter the tube. Clear nitrene solution is drawn from the bottom of *H* by means of an adjustable siphon, being collected in the bottle *I*. The nitraffin solution collects in the chamber *J;* entrained nitrobenzene drops out, and the clear nitraffin solution overflows continuously into the bottle *K*.

PLATE I.

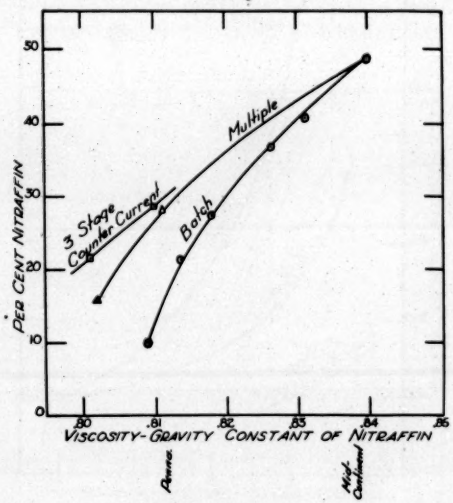


Laboratory continuous counter-current extractor.

Most untreated oils are of very dark color, although distillates are far lighter in color than residual products. Whether the compounds responsible for this deep color are naphthenic is not known; nevertheless many solvents remove a large

percentage of these color bodies with the extract, leaving the raffinate of proportionately lighter color. Nitrobenzene is particularly efficient in this respect, as may be seen by comparing the appearance (Plate I) of untreated oil, nitrene solution and nitraffin solution, as well as by noting the progressive lightening in color as the oil rises through the tube.

FIG. 5.

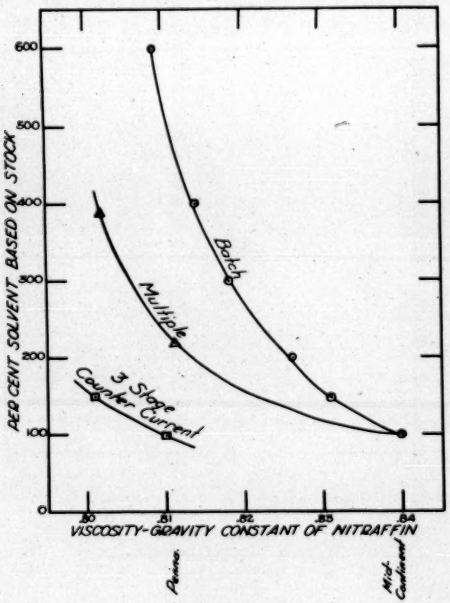


Comparison of extraction procedures.
a. Nitraffin yield.

Figures 5 and 6 illustrate the economies which may be effected over batch operation, the stock being the same as that in Figs. 2 to 4. It will be noted (Fig. 5) that multiple or batch counter-current treatment results in better yields of nitraffin of a given quality, the differences becoming proportionately greater as the quality of the desired product becomes higher. Indeed, either of these methods is capable of producing material of a quality which would seem to be impossible with a single batch treatment. Still more striking

advantages are found in the amount of solvent required (Fig. 6), 0.810 V. G. C. being produced, for example, by only 100 per cent. counter-current, whereas batch operation would require some 550 per cent.

FIG. 6.



Comparison of extraction procedures.
b. Volume efficiency.

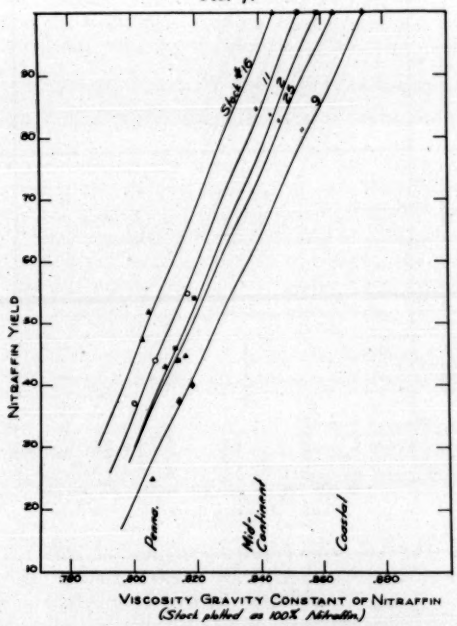
Continuous counter-current treatment would yield results slightly superior, both in respect to yield and amount of solvent required, to 3-stage counter-current. The differences are, however, not sufficient to demand such a procedure either in laboratory or plant. In the former, 3-stage batch counter-current is ordinarily employed; in the latter, provision

is made for 5 stages (continuous), which represents even a closer approach to continuous counter-current.

YIELD OF PARAFFINIC OIL FROM VARIOUS STOCKS.

The amount of paraffinic oil which can be recovered from a given stock depends, of course, upon the amount originally there. It is to be expected, therefore, that, the more naphthenic the original stock, the lower the yield of paraffinic oil. This is illustrated by Fig. 7. It will be noted that Stock No.

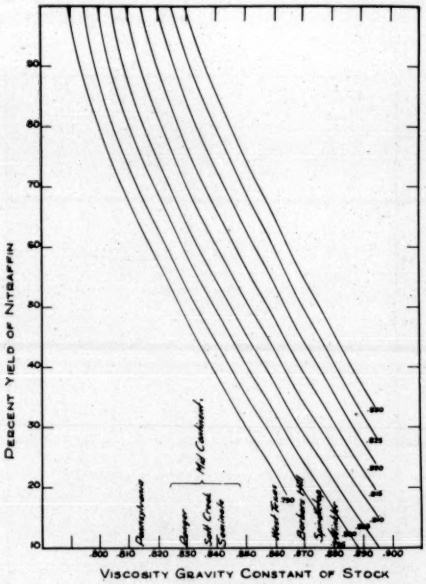
FIG. 7.



9, of .874 V. G. C., yielded only about 30 per cent. of .810 V. G. C., while stock No. 16 of .843 V. G. C. yielded over 50 per cent. of .810 V. G. C.

Figure 7 also demonstrates how similarly various stocks respond to nitrobenzene extraction, or solvent extraction in general. By reason of this similarity it is possible to construct, with reasonable accuracy, a chart such as Fig. 8, which shows what yields may be expected, from stocks varying from .800 to .900 V. G. C., of products varying from .790

FIG. 8.



to .830. The viscosity-gravity constant of the nitraffin is indicated at the lower extremity of each curve. Taking the .810 V. G. C. line as representative of Pennsylvania, some 12 per cent. of Pennsylvania quality oil may be obtained even from a .900 stock. The yield steadily increases, of course, as the V. G. C. of the stock decreases.

Figure 8 presents graphically what has already been stated,

that selective solvents make it possible for the refiner to produce oils of Pennsylvania quality from substantially any crude, and better-than-Pennsylvania from the majority. Just what crude he will select depends upon many factors. The lower the yield of the product he desires, the greater the cost of solvent extraction per gallon of finished product, but in general those crudes which give low yields are of low price. Furthermore, naphthenic crudes frequently make excellent charging stocks for the production of high-test gasoline. Whatever his final choice, he is no longer forced to buy an expensive crude in order to recover therefrom its good lubricants, and subsequently wonder how to get rid of the remainder without reducing the quality of his other products.

COMMERCIAL EQUIPMENT FOR SOLVENT EXTRACTION.

The process of nitrobenzene extraction involves the following procedure:

Stock and solvent are mixed, and cooled [4] to the temperature at which the desired separation into two phases takes place, several stages of such contacting usually being employed. After separation of nitrene and nitraffin layers, each is subjected to vacuum distillation to remove the major portion of the nitrobenzene, and is finally stripped of its last traces of nitrobenzene by means of live steam.

The equipment, like the process, is essentially simple, but it is far from inexpensive. A plant to produce 500 barrels per day of solvent extracted oil costs several hundred thousand dollars.

Figure 9 shows the method of operating a 5-stage countercurrent extractor. The charge oil is mixed with nitrene solution from No. 2 Settler (this nitrobenzene has already been used four times); chilled and charged to No. 1 Settler. The nitrene solution which settles is removed from the system (continuously), but the nitraffin solution flows to the mixer at the left, where it is agitated with nitrene solution pumped from No. 3 Settler (three-times-used nitrobenzene). From this mixer it flows to No. 2 Settler. The nitraffin solution works its way to the left, being treated with twice-used;

[4] Some solvents operate at high temperatures, and cooling is therefore unnecessary.

FIG. 9.

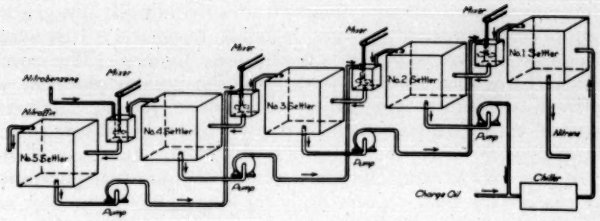
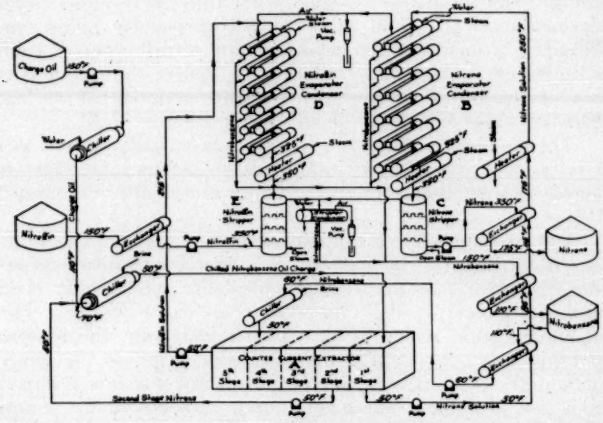


Diagram of counter-current extractor.

once used, and finally with fresh nitrobenzene coming in to the last mixer. From No. 5 Settler the nitraffin solution is drawn off. The nitrene solution works its way to the right, and finally out at No. 1 Settler.

FIG. 10.



Flow chart of nitrobenzene plant.

The remainder of the cycle is shown in Fig. 10. The nitrene solution from the 1st stage of the extractor (*A*) passes

through heat exchangers and a steam heater, being raised to 230° F., and into the vacuum evaporator-condensers (*B*). During its passage through the several sections its temperature is raised to 325° F., and all but perhaps 1 per cent. nitrobenzene is removed. Leaving the evaporator, the nitrene is further heated to 350° F., and passes, still under vacuum, through the stripper *C*, where it is brought into contact with steam, which removes the last traces of nitrobenzene.

The nitraffin from the 5th stage (*A*) goes through a similar cycle in *D* and *E*.

Germicides.—In the Wiley Memorial Lecture, H. R. L. DOHME (*Jour. Asso. Off. Agric. Chem.*, 1934, XVII, 19–28) reviews the history and value of germicides or disinfectants, agents which destroy microorganisms. The introduction and use of germicides followed the foundation of bacteriology by Koch and Pasteur and the development of the germ theory of disease. Among the earliest germicides were iodine, mercuric chloride, and phenol. Other substances that have found application in this field are lunar caustic (silver nitrate), colloidal metals, hypochlorites and chloramines, methenamine (hexamethylene tetramine), organic arsenical compounds (atoxyl, and arsphenamine and its derivatives), organic derivatives of mercury (mercurochrome, metaphen, methiolate, and mercurophen), certain dyes like acriflavine, and the alkyl resorcinols. However, "no germicide for the blood that is safe and has the approval of the medical profession is yet available." Research is now proceeding in this direction.

J. S. H.

Ascorbic Acid.—Many research workers consider that ascorbic acid, which is widely distributed in plants and animals, is a pure crystalline form of water-soluble C, the vitamin which protects from scurvy. It was formerly classed as a hexuronic acid, but its constitution has now been demonstrated by R. W. HERBERT, E. L. HIRST, E. G. V. PERCIVAL, R. J. W. REYNOLDS, AND F. SMITH (*Jour. Chem. Soc.*, 1933, 1270–1290). They used laevo ascorbic acid prepared from an animal source (adrenal glands) and from a plant source (paprica), found it to be related to the hexose sugar laevo gulose, to contain a double bond, to have the empirical formula $C_6H_8O_6$, and the structural formula

$$CH_2OH.CHOH.CH.COH=COH.CO.$$

J. S. H.

Nitrazine Yellow: A New Indicator.—HENRY WENKER (*Ind. and Eng. Chem. Ind. Ed.*, 1934, XXVI, 350) suggests the use of nitrazine yellow (2, 4-dinitrobenzene-azo-1-naphthol-3, 6-disulphonic acid) as an indicator. This compound dissolves in water to produce a red-brown solution, the color is bright yellow in acid solution, and a bright deep blue in alkaline solution. It is yellow at pH 6.0, pale yellow at pH 6.4, pale gray at pH 6.6, pale blue at pH 6.8, and blue at pH 7.0.

J. S. H.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

HAIRSPRINGS OF WATCHES.

In RP670 in the April *Journal of Research* the performance of watches having the usual cut, bimetallic balance wheels and steel hairsprings is compared with that of watches having uncut, monometallic balance wheels and elinvar hairsprings. The latter combination of vibrating assembly is a new application intended to improve the general performance of watches.

Twenty watches of each type, ten each of two makes, were given performance tests at temperatures encountered in ordinary use. The temperature-rate errors of the watches having the new vibrating assembly were less than those for watches having the ordinary assembly, and instead of the usual parabolic curve, a curve approaching a straight line was obtained. Marked improvement in performance at temperatures within the usual range 0 to 50° C. is indicated by the use of the new assembly.

The new assembly almost entirely overcomes the effects of magnetism, so that, after the watch is removed from a magnetic field, the rate is not subject to fluctuations experienced with the ordinary assembly.

There is no evidence of any marked difference in performance of the two types of watches in different positions or for isochronism.

FIRST SPECTRUM OF TANTALUM.

Although the element tantalum has been known to chemists for over a century, it is only in recent years that it has been prepared in quantity in its uncombined state, largely through the efforts of Dr. C. W. Balke of the Fansteel Company. Tantalum possesses many physical and chemical properties which, through the rôle they play in the arts and industries, have made it a very useful member of the

* Communicated by the Director.

family of metals. Modern analytical methods require a knowledge of the atomic energy states of an element, and this can be obtained only from analyses of the term structures of the spectra emitted by the element in its various states of ionization. The collection of the necessary data for the solution of such a problem is part of the program of the spectroscopy laboratory of the Bureau. In the case of tantalum much of the experimental work has been completed, but much yet remains to be done in the way of calculation and analysis. As a first contribution toward the completion of the work a description has been published in the April number of the *Journal of Research* (RP671) of the spectrum emitted by neutral or un-ionized tantalum atoms when they are excited by the arc in air. The electrodes used in this work were cut from a rod of the metal prepared by Doctor Balke and presented by him for this investigation. More than 2100 wave-lengths of tantalum lines have been measured in the interval extending from 10,300 A in the infrared to 2300 A in the ultraviolet. This spectrum is superposed on an extensive band spectrum emitted by molecules of tantalum oxide which are always present in the light source. Many of the tantalum lines appear as narrow rectangles and show evidence of being composed of several closely-packed lines. Hyperfine structure of this type has been recognized and measured for many of the elements, and from it important information about the nucleus of the atom is derived.

THERMAL CONDUCTIVITY OF METALS.

It is a familiar fact that metals are good conductors of heat, and that certain metals, such as copper and aluminum, conduct heat much more readily than other common metals such as iron and steel. Numerical data on the heat conductivities of various metals and alloys have important theoretical and practical applications. RP668 in the April number of the *Journal of Research* describes a method and apparatus for the accurate determination of thermal conductivities of metals and alloys up to a temperature of 600° C. (1112 F.).

In the method employed, the conductivity of a metal is compared, either directly or indirectly, with that of lead.

Lead was selected as the standard since previous measurements have established its conductivity within fairly close limits. Determinations are made by measuring the axial temperature gradients in two cylindrical bars soldered together end to end, one end of the system being heated and the other cooled, and the convex surfaces protected from heat loss by a surrounding guard tube.

To determine the accuracy of the apparatus, a series of experiments was made with three metals, lead, zinc, and nickel. The conductivity of each metal was compared with that of each of the other two, and all results obtained were consistent within 2 per cent.

Data are also given in the paper on the thermal conductivities of several commercial nickel chromium and other alloys widely used for electric heating elements and thermocouples.

THERMAL CONDUCTIVITY OF IRONS AND STEELS.

Most of the researches on the thermal conductivity of metals were made in an attempt to correlate their thermal and electrical conductivities. There have been surprisingly few determinations of the thermal conductivity of irons and steels, the most widely used of all metals. While the actual thermal conductivity of a structural metal may seldom be the most important factor to be considered in selection or design, the thermal conductivity of structural materials over a range of temperature is of considerable importance in many instances.

The Bureau has recently completed determinations of thermal conductivities of 20 miscellaneous irons and steels over the temperature range 100 to 500° C. (212 to 932° F.). The materials were selected as typical examples of commercial materials used for a variety of purposes and were expected to differ considerably in thermal conductivities. They included cast irons, carbon and low-alloy steels, high chromium and manganese alloy steels, and "18–8" type of stainless steel.

The results, which are published in the April *Journal of Research* (RP669), show that the differences in conductivity of irons and steels are much smaller at high temperatures

than at room temperatures. High-alloy steels have lower thermal conductivities than low-alloy steels. An increase in the amount of alloy constituents in iron causes, in general, an increase in the temperature coefficient of thermal conductivity.

CREEP OF METALS AT ELEVATED TEMPERATURES.

Solid metals may flow or "creep" if they are subjected to a constant or continued load, which behavior is particularly noticeable when the metal is at a temperature above normal atmospheric temperature.

In studying the "creep" of metals, the Bureau has prepared single crystals of silver and has been measuring the very slow flow or creep of these single crystals when sustaining constant loads at 400° C. With this type of specimen the influence of the grain or crystal boundaries on the creep of metals is eliminated. Some of these single crystals have now been under load and slowly creeping for over nine months. The rate of creep of a silver crystal at 400° C. is influenced by the direction of the stress in the crystal relative to the crystal axes. The rate of creep is relatively low when the load acts in a direction approaching that of a perpendicular to the cube face of the silver crystal. The rate of creep is distinctly higher when the crystal is loaded in a direction making an angle of 30° to 45° with this same perpendicular.

WEATHERING OF SHEET ALUMINUM ALLOYS.

The investigation of the corrosion of aluminum alloy sheet materials has been in progress at the Bureau since 1925. Its purpose is to study and develop methods for the elimination of corrosion-embrittlement in the alloys utilized in aircraft, more particularly duralumin.

Extensive laboratory corrosion tests, supplemented by actual exposure of specimens to the weather at Washington, D. C., Hampton Roads, Va., and Coco Solo, C. Z., have furnished data on the behavior of these materials under conditions conducive to corrosion.

Corrosive attack of the intercrystalline type is most undesirable in sheet aluminum alloys, since it results in

serious embrittlement. The attack is particularly insidious because it may be difficult to discern on the surface even when it has penetrated the metal deeply, following the path of the crystalline, or grain, boundaries. The results of tests have indicated that intercrystalline attack in sheet duralumin may be practically eliminated if certain procedures are followed in heat treating the material. The heat treatment recommended involves heating at a temperature closely approximating 505° C. and quenching quickly in a medium conducive to rapid cooling, such as *cold* water.

Reheating of heat-treated duralumin at temperatures between 100° and 300° C. renders the material susceptible to the intercrystalline attack. This attack tends to penetrate sheet duralumin much more rapidly than the usual pitting. The latter develops in material which is properly heat-treated and tends to spread on the surface rather than to penetrate. Losses in the tensile properties, after the same length of time of exposure to the weather, are much greater with material that is susceptible to the intercrystalline attack than with material on which only pitting is present.

Slight differences in chemical composition or small amounts of cold-working are less important in influencing the rate of corrosive attack than is the method of heat treatment. Invariably, corrosive attack, as evidenced by the loss in tensile properties, proceeds at its most rapid rate within the first two years of exposure to the weather. Thereafter, to the conclusion of a 5-year exposure period, further losses in tensile properties were seldom in evidence.

Saline or marine conditions of exposure resulted in a much more rapid initial rate of corrosive attack and indicated the need for protective coatings under these conditions. Surface coatings of high purity aluminum, especially those of a type integrally alloyed to the base metal of the sheet, served excellently in retarding corrosion under severe conditions.

The general conclusion arrived at as a result of the tests was that aluminum alloy sheet materials are to be regarded as thoroughly reliable from the standpoint of their permanence in service, provided proper precautions are taken to render them corrosion-resistant.

COMPRESSION CUTTING TEST FOR RUBBER.

A common method of measuring the quality of a rubber product is to make tensile strength and stretch tests on specimens of the rubber used. For products such as rubber bands, these tests are closely related to actual service, but for many rubber products, such as insulated wire, hose, and tires, the tests have only an indirect bearing on the performance in service.

In an attempt to make a test which would approximate the conditions encountered in use by many rubber articles, and at the same time simplify testing, a compression cutting test was suggested by the Bureau. This test consists of compressing a sample of rubber to failure between a flat plate, or anvil, and a cutting tool and recording the relation between the thickness of the sample and the load up to failure. The Bureau has recently completed a detailed study of this test. The results are described in the April number of the *Journal of Research* (RP674) in which the conclusion is reached that the compression cutting test is valuable as a supplement rather than as a substitute for tensile strength and stretch tests.

THERMAL EXPANSION OF ALPHA, BETA, AND ZETA ALUMINA.

The values for linear thermal expansion were obtained by the interferometer method, using a heating rate of approximately 2° C. per minute. The alpha alumina was taken from a mass of special "white" corundum as manufactured for the abrasive industry. The beta alumina was furnished by the Norton Company and was in the form of well developed plates measuring as much as 1/2 inch in maximum dimension. The zeta alumina was made by H. B. Barlett and obtained as relatively minute crystals which were wetted with a dilute solution of aluminum chloride, specimens formed, and heated at 1550° C. The determinations for the alpha and zeta forms therefore are not referred to any particular crystal axes, but gave average values. Furthermore, because of the extreme friability of the zeta alumina specimens and the consequent difficulty of obtaining accurate measurements of the height of the specimens, the data for this form are considered approximate only. The results are summarized in the table.

Form of Al_2O_3.	Average Coefficient of Linear Thermal Expansion [a] for Temperature Range of:					
	Room Temperature to 200° C.	200° to 300° C.	300° to 400° C.	400° to 500° C.	500° to 600° C.	600° to 700° C.
alpha	7.0	7.3	8.1	8.5	8.8	9.2
beta [b]	5.1	6.2	6.0	5.8	5.7	6.0 [d]
[c]	5.7	7.0	7.2	7.5	7.7	7.6 [d]
zeta	6.0	7.1	7.7	8.8	8.5	7.7 [d]

[a] Values to be multiplied by 10^{-6}.
[b] Parallel to C axis.
[c] Perpendicular to C axis.
[d] Values to be questioned because of reaction between specimens and silica plates.

TALC IN SAGGER BODIES.

A short study of the effect of magnesium oxide, added either as pulverized talc or magnesite, on the physical properties of a sagger body included the determination of refractoriness as expressed in pyrometric cones, the linear thermal expansion, the modulus of elasticity and transverse strength at room temperature and at 625° C., the plastic deformation under load at 1200° C., and the absorption. The results of studies already reported have led to the conclusion that information on those properties was the most significant when attempting to estimate the service life of sagger bodies.

Both talc and Grecian magnesite were tried in these tests to determine (1) whether it was the magnesium oxide which caused changes in certain of the physical properties of the body, and (2) whether the magnesium oxide could be added in the form of either talc or magnesite in order to obtain the desired results. The talc used contained approximately 11.5 per cent. wollastonite, 1.5 per cent. calcite, and the remainder magnesium silicate. The quantities of magnesite added to the body contained magnesium equivalent to the magnesium in the corresponding talc-containing bodies.

The P.C.E. (softening point) of the commercial sagger body used in the test was 27–28 (approximately 1610° C.). When 2.5 per cent. talc was added the P.C.E. was 23; and with 5 per cent. talc 18–19 (1500° C.). Bodies containing corresponding amounts of magnesium but in the form of

magnesite had a P.C.E. of 26 (1595° C.) and 20–23 (1550), respectively. The total linear thermal expansion in per cent. at 1000° C. for the magnesium-free body was 0.592; that with 2.5 per cent. talc 0.535; with 5 per cent. talc 0.462. Corresponding bodies containing the magnesite showed 0.525 and 0.470, respectively.

The modulus of elasticity at room temperature expressed in 1000 lb./in.^{2} for the magnesium-free body was 1125; for the 2.5 per cent. talc-containing body 765; the 5 per cent. talc 555; for the bodies containing equivalent percentages of magnesium but in the form of magnesite, 615 and 525, respectively. The modulus of rupture in lb./in.^{2} for these five bodies was 630, 615, 480, 475, and 515, respectively.

The total plastic deformations (in inches) at the end of $2\frac{1}{2}$ hours, at a temperature of 1200° C., and with a constant load of approximately 6 lb./in.^{2} placed at the center of a 1″ x 1″ x 9″ specimen over an 8-inch span, were as follows: sagger body without addition of talc or magnesite, 0.071; the 2.5 per cent. talc body 0.039; the 5 per cent. talc body 0.062; the corresponding magnesite-containing bodies 0.023 and 0.0235, respectively.

The absorption ranged between 14 and 15 per cent., the lower value being obtained in the body containing 5 per cent. talc.

Gaging the service life of the sagger from the

$$\frac{\text{modulus of rupture}}{\text{modulus of elasticity}}$$

values, together with the total linear expansion at 250° C., it was found that with respect to resistance to thermal shock any one of the bodies containing either added talc or magnesite should have a much longer life in service than the body containing none. Actual plant records on the 2.5 per cent. talc body in comparison with the talc-free body indicated the latter to have approxi nately one-half the life of the former.

The plastic deformation (bulging of sagger bottoms) of the sagger body is decreased when measured under the conditions stated, by the addition of either talc or magnesite to the body.

The limited amount of data obtained on the sagger body tend to show that (1) either talc or magnesite may advantageously be used in sagger bodies; (2) magnesite is preferable to talc; (3) 2.5 per cent. talc is probably more desirable than 5 per cent., but the same does not hold true for magnesite.

The effect on the properties of a finished sagger will naturally depend on the type and purity of the talc or magnesite added to the body from which it is made.

Boiling Point of Fluorine.—WILLIAM H. CLAUSSEN (*Jour. Am. Chem. Soc.* 1934, LVI, 614–615) calculates that the boiling point of fluorine is 85.21° K., "a value correct within 0.1°."

J. S. H.

Atomic Weights of Carbon and Iodine.—GREGORY PAUL BAXTER AND ARTHUR HAYS HALE (*Jour. Am. Chem. Soc.*, 1934, LVI, 615–617) have studied the ratio of iodine pentoxide to sodium carbonate. They conclude that the atomic weight of iodine probably is not higher than 126.92, and that the atomic weight of carbon probably is higher than 12.00.

J. S. H.

Philadelphia Drinking Water.—GEORGE G. SCHAUT (*Jour. Am. Water Works Asso.*, 1933, XXV, 1287–1294) has made a study of the lactose-fermenting organisms in the municipal water supply of Philadelphia. He concludes that these organisms "to the extent shown in this study, in a properly purified and chlorinated water have no sanitary significance as far as the health of the city is concerned." These organisms are most efficiently removed from the water by long, preliminary sedimentation, followed by slow sand filtration. Next in efficiency is short sedimentation followed by double filtration, using rapid sand pre-filters and slow sand final filters. The least efficient procedure is a plain rapid sand filter. Prechlorination and postchlorination plus rapid sand filtration is of no avail. The efficiency of the filter is influenced by the temperature of the water. The occurrence of these organisms is not influenced by yearly climatic conditions or by the mineral characteristics of the water.

J. S. H.

THE FRANKLIN INSTITUTE.

FORMAL OPENING AND DEDICATION OF THE LIBRARY OF THE FRANKLIN INSTITUTE, FRIDAY EVENING, FEBRUARY 23, 1934.

PROGRAM.

Introductory remarks—Dr. Walter T. Taggart, Chairman of the Committee on Library, Presiding.

The Place of the Special Library in City Life—Miss Mary Louise Alexander, President, Special Libraries Association, New York.

Research Libraries and Popular Libraries—Dr. E. C. Richardson, Special Librarian, The Library of Congress, Washington, D. C.

What the Library of The Franklin Institute has Meant to Me—Mr. F. Lynwood Garrison, Philadelphia.

Remarks by the Librarian, Mr. Alfred Rigling.

Dedication of Pepper Hall in honor of George Wharton Pepper, Esq.

The meeting was called to order in the lecture room at 8:30 o'clock by Dr. Walter T. Taggart, Chairman of the Committee on Library of The Franklin Institute.

DR. TAGGART:

After one hundred and eight years of continued active service in our old home on South Seventh Street, we have come together to dedicate our magnificent new Library Hall in honor of the George Wharton Pepper, Esq. whose services to The Franklin Institute are indelibly written for all time.

As Chairman of the Library Committee, it is an honor and privilege to represent my colleagues on this happy occasion.

It is not my purpose to give a history of the Library of

The Franklin Institute or the JOURNAL OF THE FRANKLIN INSTITUTE, through which this venerable institution is known throughout the world.

It is my firm belief that The Franklin Institute, through its journal, is better known abroad than any similar institution in the United States.

May I remind you that it is to the persistent efforts of Samuel Vaughan Merrick, then but 21 years of age, that this Institute owes its origin.

The meeting for organization was held on February 5, 1824, at the Old State House, Sixth and Chestnut Streets. The hall was crowded to overflowing.

James Ronaldson, Esq., was elected President and served in that capacity for 17 years; he was succeeded by Samuel Vaughan Merrick who served as President until 1854.

The Franklin Institute of Pennsylvania was chartered March 30, 1824, and in the Act of Incorporation its object was defined to be "the Promotion and Encouragement of Manufactures and the Mechanic and Useful Arts." It was intended to be a democratic institution.

The original organization included Standing Committees on Instruction, Inventions, Premiums and Exhibitions, Library, Models and Minerals.

The first course of The Franklin Institute lectures on Chemistry was delivered by Professor William H. Keating at the Old Academy at Fourth and Arch Streets with the permission of the Trustees of the University of Pennsylvania. The first exhibition of American Manufactures was held in the Autumn of 1824 at Carpenter's Hall under the auspices of The Franklin Institute and was crowned with complete success.

The Institute has held about thirty exhibitions since that time.

The largest and most important exhibition was held in 1874 at the old Pennsylvania Railroad Freight Station at 13th and Market Streets where John Wanamaker's store now stands. In five weeks there were about 270,000 paid admissions and a net profit of over $52,000.

In 1884 The Franklin Institute held the first International Electrical Exhibition at the old West Philadelphia Penn-

sylvania Railroad Station at 32nd and Market Streets. This exhibition also was a great success.

The present exhibition in this building tells its own story—the story of the advance of science and technology in action. It will continue to develop with the ages. In the 110 years of the Institute's life there have been numerous efforts to seek larger and better quarters; first in 1837, again in 1838, and also in 1870.

By act of City Councils in 1868 it was decided to build a City Hall on Independence Square; the popular opposition was so great that the plan had to be abandoned.

In 1870 a new plan was submitted to the citizens to decide whether Washington Square or Penn Square should be the site for the new City Hall. It was understood that if Washington Square were chosen for the City Hall site, then The Academy of Fine Arts, The Academy of Natural Sciences, The Franklin Institute, and The Philadelphia Library were each to be given permission to build on one of the four quarters of Penn Square.

The people decided by a vote of about 50,000 to 30,000 in favor of the present site of City Hall but no provision was made for the above institutions on Washington Square.

Is it not remarkable that three of these four institutions should today be located about Logan Square on the Parkway and that the Philadelphia Art Museum should grace the Parkway at one end and City Hall at the other?

Philadelphia is rich in special libraries; the first of these, mainly relating to pure and applied science, was founded in 1743 by the American Philosophical Society.

We are now to have the pleasure of hearing from the President of the Special Libraries Association. I take pleasure in presenting Miss Mary Louise Alexander, who will tell us about the "Place of the Special Library in City Life."

Miss Alexander:

It is a very real privilege to take part in this program tonight and a personal pleasure to bring to you the official greetings of the Special Libraries Association. Mr. Rigling holds a place of great importance in our association—as head of one of our largest chapters, as librarian of this fine and

famous library of The Franklin Institute and as dean of the special library profession. I feel safe in using that term because I am sure no other member can boast as many as fifty years' service to the same organization. It is a great temptation to dwell on the achievements of Mr. Rigling and of this Institute but those who follow me can do that far more adequately than I.

The subject assigned to me is "The Place of Special Libraries in the Life of the City." I cannot claim to know Philadelphia intimately since my own work has always been in New York, but as president of S. L. A. for two years I have kept closely in touch with the activities of our thirteen local chapters scattered across the country and I am sure that in proportion to their number, special libraries everywhere play much the same rôle.

First I suppose that I should define a special librarian because I find great confusion in the minds of many as to who we are and what we do. A special library is one devoted to a special interest; it serves a restricted clientele such as a bank, a newspaper, a group of engineers, or a business corporation. It is in charge of an expert who is thoroughly familiar with the subject the library covers. I think that if there is one distinction that special librarians can claim it is that we know our source material intimately. We do not simply collect, sort and catalog information, but we put that information to work. An understanding of the problems of the people we serve allows us to undertake research and supply the answers to questions instead of simply supplying the material from which others get the answer. This routine is in contrast to that of a public library which must of necessity serve everyone alike, and can seldom afford to devote time and money to intensive service for a special group. Many public libraries are developing separate departments such as business branches, municipal reference departments, etc., and these are considered special libraries. They form an important section of our association.

One of the most interesting things about our profession is its great variety. In our membership of 1600 we have libraries covering all phases of our modern life. The cultural side is represented by important art and museum libraries as

well as music collections; civic subjects by the many governmental libraries in Washington as well as the municipal libraries in all the large cities. Newspapers which obviously play an important part in the affairs of a city are served by large and active libraries. Scientific and technical libraries are numerous and of many kinds, as chemical, electrical, automobile or engineering libraries. Research organizations of all sorts profit by having their own library service. And last but not least, there are the business libraries which represent the largest group in our association. This group includes bank libraries, those of insurance companies, advertising agencies and business corporations of all sorts. Surely this is a cross-section of our modern life.

Varied as are the above interests, special libraries have made only a beginning in any of these fields. While our association knows of perhaps 250 bank libraries in the country, there are more than 20,000 banks in the United States. We have a record of some 300 newspaper libraries, but there are at least 2000 papers printed in the large cities of this country. Only 75 insurance companies out of more than a thousand have yet installed their own library service. And while we know of more than 600 private business libraries there are, of course, literally thousands of business corporations that have yet to organize a library. As the depression lifts, the profession expects a great increase in the development of special libraries. Important economists and business men are pointing out the economy of profiting by the experience of others and making use of the wealth of information available. The New Deal calls for economic planning, the new competition will demand better production methods, the use of new materials, the development of new products. All of these call for the intensive use of basic information and for increased research.

As added proof that special libraries have a place in the sun, a nice thing has recently happened to the Special Libraries Association—a money grant from the Carnegie Corporation of N. Y. Under the New Deal, trade associations everywhere have been given a new responsibility and new importance. Relatively few of these have organized libraries and it is necessary to build up their facilities quickly. S. L. A.

is peculiarly fitted to help these associations since our members control reservoirs of information and have had specific experience in the fields covered by trade associations. We are pleased that the Carnegie Corporation approved and are sponsoring our plan to develop library service for trade associations. This project is of special importance to you in Philadelphia because Miss Dorothy Bemis, librarian of the Lippincott Library at your University of Pennsylvania, has been chosen to direct the work. We plan to contact associations and offer them help in organizing current information or in finding a trained librarian or in giving any type of research service. We hope for the interest and help of the entire profession.

A project such as the Carnegie grant helps to educate the public as to the service special libraries can render. This dedication of The Franklin Institute Library helps the movement too and is also good for the morale of special librarians everywhere. Such a library makes us doubly proud of our profession. Again let me say that it is a privilege to pay the official respects of the Special Libraries Association to Mr. Rigling and The Franklin Institute.

DR. TAGGART:

Our next speaker is Special Librarian in the Library of Congress at Washington, D. C. For a number of years he was Librarian at Princeton University.

This reminds me that the Smithsonian Institution which was established in 1848 had for its first Secretary that great American physicist, Joseph Henry, formerly Professor of Physics at Princeton University. You will also be interested to know that Mr. Richard Rush, a Philadelphia lawyer and a graduate of Princeton, went to England, to represent the United States Government, and brought back with him over $500,000 from the James Smithson estate to establish the Smithsonian Institution.

It now gives me pleasure to present Dr. E. Cushing Richardson, Special Librarian of the Library of Congress, who will address us on Research Libraries and Popular Libraries.

DR. RICHARDSON:

The topic assigned to me this evening was not a subject in the field of librarians. In view of the fact that all of this was in honor of Benjamin Franklin, I was reminded that Benjamin Franklin was the founder of American popular libraries. I therefore, choose the topic

Research Libraries and Popular Libraries.

The Franklin Institute Library is a research library. This means that its aim is to aid in the production of new ideas, not their dissemination. It promotes invention or discovery. The end of research is a new idea. This original idea is unique. It exists, for a time, only in one mind.

Popular libraries, on the other hand, stand at the opposite pole. They have to do with common knowledge or general reading, as distinguished from the libraries of learning, higher education and research. The object of the popular library is not to produce ideas but to multiply them. It takes new ideas and turns them into commonplaces, or common knowledge. Its ideal end is the reproduction of a given idea in the mind of every human being—a perfectly commonplace idea.

These two objectives are as far apart as the poles, but they are interdependent, not independent. The north pole cannot say to the south pole, "I have no need of thee." Neither can function without the other. Each without the other is without existence.

Several times lately leaders of the popular library activities of the American Library Association have declared that the Association cannot undertake the promotion of service for research libraries, because only a small fraction of the membership is "concerned in any direct way" with the research library service problems. The latest version refers to cataloging service and makes the ratio one to thirteen, "not more than one thousand out of thirteen thousand members" it is said.

The catch in this statement lies in the word "direct." Everyone acknowledges that popular libraries are indirectly concerned with the effectiveness of the research libraries.

As a matter of fact, however, even the statement as to "direct" is probably a numerical error. More likely, only

one out of thirteen members of the A. L. A. is *not* directly concerned with the services of the libraries of learning, reference or research, and possibly thirteen out of thirteen are so concerned—slightly perhaps but yet directly.

In the first place, almost every library has a few rare books, or at least one. It has also a certain number of books which for one reason or another are difficult cataloging. The small popular library cannot afford a trained cataloging staff for doing these. It must and does look to the printed cards of well-staffed libraries. More than six thousand libraries use such cards.

Again, every popular town or city library which caters to the needs of doctors, ministers, lawyers, engineers and school-teachers, as well as to the general reader, gets more of the same benefit, and if it caters to the local historians and genealogists, as most public libraries do, and all ought to, they are concerned with the same type of cataloging and study method as research libraries generally. They are, in fact, themselves research libraries of a sort, and their librarians need to be trained in the methods and tools of research work. Such training is a matter of direct concern. Every such library is therefore vitally concerned, even though this concern is on a smaller scale and the new ideas are not such as to set the world afire.

Yet again: in the case of the very large class of small college libraries, the matter is obviously of direct and deep concern. Almost every member of the faculty of such colleges is, or should be, engaged in some research work, in order to keep his soul alive. Many of them realize it, and the librarians must operate many of the methods of research library service, not only in cataloging, but in information service. It is characteristically for the benefit of these small libraries that the methods of inter-library borrowing have been developed. University libraries use it more, but the smaller libraries are more dependent upon it. And very many of the smaller libraries contribute their reciprocal mite to this service which is coördinated by the Library of Congress Union Catalogue. What applies to the small college library, applies also to many secondary and public school libraries to a degree. With the modern development of interest in

research studies, there is always a chance nowadays too that even the smallest town will have a minister, a doctor or a school teacher who is a Ph.D., or has some unfulfilled ambition in specialized scientific production. The librarian of such a town is directly concerned in knowing how to borrow research books for his client, and what kind of books to contribute to the Union Catalogue in order to do his reciprocal share.

Altogether, one wonders whether there is any library in these United States of America, which is not directly concerned with research library efficiency.

As for the "indirect" concern, no one can well deny that popular libraries, whether directly or indirectly, are vitally concerned with the work of the research library, for the life of such libraries depends on the quality of their books, and this quality in turn depends on the quantity of fresh ideas in them. When ideas, once fresh, have been reduced to complete commonplaces in the mental possession of every reader, interest, of course, ceases. It is the fresh ideas which are the life of a man, a library, a community or the world, and it is research which furnishes the fresh ideas. Popular libraries without the new ideas which they owe to research workers, are dead.

So much for the coöperative dependence of popular libraries on research libraries.

Turning now to the reciprocal dependence of research libraries on popular libraries, it may be remarked that this dependence is less obvious and possibly less "direct," but it is no less real. The evolution of ideas, like the evolution of all other living things, is closely related to the multiplication of the species. The greater the number of copies the better the chance for one of them to fall on good soil and produce some useful variation of the idea, that is, some variation which tends to keep the idea alive in the struggle for existence, where other copies perish. The oak produces thousands of acorns to one which becomes an oak. The greater the number of copies produced and the wider their dissemination, the better the chance of a favorable variation and survival. This dissemination is the task of the popular libraries.

Most or all original ideas which come under the head of

inventions are the outcome of this multiplication and survival. For instance, the latest patents on this or that idea in applied electricity, contained in the collection of patent records, which is the most distinguished specialty of the Library of The Franklin Institute, are not creations out of nothing, they are laborious accumulation of a vast number of useful variations of previous ideas, resulting from the wide dissemination of those ideas, and the taking on here and there of favorable variations or "improvements" of the idea.

When I was a boy haunting the local public library, one of the most vivid, stimulating and abiding impressions of a lifetime was registered in a mental image from a rough wood-cut in an account of Benjamin Franklin, of the great researcher standing out in a storm with a kite and a key, preparing to send up the key into the clouds to collect lightning stuff. Ten years later they showed us in college a spark passing from one carbon point to another, and they let us listen into a fruit can in Walker Hall to some indistinct words from another fruit can in North College, coming over a connecting wire. In both cases the professor, a recent and brilliant pupil of the famous Helmholtz, carefully explained that you never could expect these to be anything more than playthings, because of inherent and insurmountable physical difficulties. Night before last in a room exquisitely lighted by electricity, I heard on the radio a well-executed vocal and instrumental rendition of a selection from an Italian opera.

It is a far cry from Franklin's key to the radio and the smashing of atoms by incredibly powerful electrical machines, but the progress from the one to the others has been a natural and constant cycle of the forming of new ideas, multiplication, survival and reintegration. This is the history of all ideas, patentable or unpatentable.

The task of making a new idea into common knowledge begins with systematic education. Higher education seizes on the new ideas and imparts them to especially apt and trained individuals, at the same time teaching the students how to find such ideas for themselves. This aristocracy of learning in turn passes on the ideas by means of secondary education, libraries, the common schools, adult education, journalism, the radio, the club, the corner grocery, the soap

box and what not, until every normal mind is equipped with the once new idea—say that idea that flint and steel striking together will produce a spark. Then variations appear, and the task of the researcher and the research libraries begins. What they do is to gather diligently all variations of the idea for the use of the specialist who, to begin with, equips his mind with these. His mind is the alembic in which the variants are fused into a new idea. The task of the library stops with the gathering of the records. The task of the researcher goes on from this. When the variants have been gathered in the mind of some man with high powered energy they do somehow fuse. This highest mental energy we call genius. Some fancy this as human, some think it superhuman. Some even call it electric. At all events it works like an electric furnace. Many variants of the same idea go into it, a new idea comes out containing all the values of all the variants fused in one.

Benjamin Franklin's mind was one of these high powered alembics. It produced among other new ideas, one in the field of popular libraries, one in electricity. Directly and indirectly these two ideas produced the Philadelphia Free Public Library and The Franklin Institute Library—twin factors of farther progress of human ideas.

DR. TAGGART:

We are now to hear from one who has been a member of the Institute since 1887, a member of the Library Committee for over a quarter of a century, formerly its Chairman, a member of the Board of Managers for eleven years and one of the best informed members on the history and activities of the Institute. By profession he is a Consulting Mining Engineer. It gives me great pleasure to present my colleague, Mr. F. Lynwood Garrison, whose topic is "What the Library of the Franklin Institute Has Meant to Me."

MR. GARRISON:

Mr. Chairman, members of the Franklin Institute, Ladies and Gentlemen:

In relating to you some of the incidents connected with the history of The Franklin Institute with which I had to

do forty or more years ago, it will be necessary for me to be quite personal, I hope however not to bore you.

My first interest in the Institute began in the year 1886 upon the receipt of a letter from the Secretary asking me to call to see him. At that time although, of course like all Philadelphians I had often heard of The Franklin Institute, I was almost wholly unacquainted with the character of its work and its personnel, in fact I had to inquire regarding its exact location. As the result of my acceptance of this request I met for the first time its genial secretary Dr. William H. Wahl and began a friendship which lasted until his death. His kindly and cultured influence upon me, a very young man recently returned from his studies abroad, had a decided effect for good upon my future life and work and I would fain take this opportunity to pay tribute to his memory so indissolubly connected with the history of this venerable institution.

The purpose of Dr. Wahl's invitation was to ask me to deliver a lecture before the Institute upon some microscopic investigations I was making upon iron and steel and which had been the subject of a paper I had read before the American Institute of Mining Engineers not long previous to my visit to him. Naturally I was both surprised and pleased by such a flattering attention. I might explain in this connection, that I was the first person in the country to take up this interesting subject now part of the curricula of practically every technical school and college in the world and known as "metallography," the microscopic structure of metals. The lecture was given and in due course appeared printed in the JOURNAL so I had reason to suppose I had not done so badly. At any rate I was shortly asked to join the Institute and subsequently wrote several other papers on cognate subjects. Early in the year 1889 the Institute was requested to send a representative or delegate to the International Exhibition to be held in Paris that summer. I was asked if I would care to accept this appointment without compensation and provide for my own expenses as the Institute had no money for that purpose. I naturally hesitated a long time before accepting on account of my youth and inability to see my way clear to find the needed funds. The opportunity however was so alluring I

decided to pay them myself and a commission dated May 1, 1889, was handed me with instructions "to examine and report upon subjects pertaining to the Metallurgical Arts" in France.

On arriving in Paris I found I would have to work under the direction of the United States Commissioner General Wm. B. Franklin, a distinguished Civil War veteran. Fortunately for me I knew the General and his family, having visited their home in Hartford, Conn., and was accorded a cordial welcome. The work which I had lightheartedly set out to do proved more of a task than I expected, but after a short walking trip in Switzerland I buckled down to it with the result that after I returned home I was able to complete a report which covered 114 pages of THE FRANKLIN INSTITUTE JOURNAL. On the heels of this work followed a request that I give two lectures at the Institute on the subject of "New Alloys" then coming into prominence in the metallurgical industries. This was done on the evenings of January 30, 1890, and February 6, 1891. Following this in 1891 came a request from the "Bureau of Ordnance of the Navy" that the Institute send a representative to attend the armor plate trials to be held in the autumn of that year at the Indian Head proving ground on the Potomac River in Maryland. The purpose of these trials was to determine the best type of armor plate for our then new ships, and their relative resistance to the impact of projectiles, which involved a high degree of metallurgical and chemical investigation as well as mechanical methods of manufacture. In order to make this report intelligible to the general reader it was necessary to include in it a historical sketch of the development of armor plating on ships which began shortly before our Civil War. I could not have done this research work if I had not had at my command this splendid library we are here tonight to rededicate. As I recall the matter, these trials covered three or four days and I was obliged to pay my own expenses but the report appears to have been a success for it was subsequently translated into German and I think also into French, but of that I am not sure.

As a result of these various activities in behalf of the Institute I became a member of the Library Committee in

1891, serving until 1902; in 1898 I was elected its chairman; I was made Professor of Mining and Metallurgy of The Franklin Institute, serving from 1893 to 1904, and chairman of its "Section" on Mining and Metallurgy without any emoluments. Later I was elected a member of the Board of Managers, upon which I served eleven years (1890–1895, 1897–1903). It was during this period of service the Institute passed through some of the most trying years of its history. It was so straitened for funds to conduct its work it was seriously thought we might be obliged to close its doors. However, through the unselfish devotion of its secretary, Dr. Wahl, and others we tided over the crisis and things began to improve. A group of wealthy and prominent men were elected to the Board of Managers, mostly friends and acquaintances of my own, and our future seemed better assured; a steel stack was built into the front section of the old building and we were enabled to store the best part of the valuable books where at least they would be comparatively safe from fire. Small bequests or trust funds began to drift in for the maintenance of the library and it slowly began to assume its rightful place as probably the second if not the first of engineering libraries in this country. This was before the libraries of the great national engineering societies in New York City had been consolidated as they are at present.

In January 1900 I was sent to China as engineer of a British mining company and from that time on my active participation in the work of the Institute was necessarily curtailed and practically ceased. I had married and the needs of wife and small children required substantial emoluments. Hence I had little to do with its subsequent activities, although my interest has never ceased.

On my return from South Africa a few years ago I heard that the new Secretary, Dr. Howard McClenahan, had performed a miracle, had raised a fund of five million dollars for a new building and fitting memorial to the illustrious Franklin at a time when the whole country appeared sinking into a financial abyss. Naturally I inquired who was this remarkable man and was told he was an erstwhile dean of Princeton University, a distinguished physicist and man of letters. For myself whatever else he may be, I think him a veritable

Aladdin with a magic lamp and ring to conjure up the genii to build this beautiful structure that you will inspect tonight, something vastly greater, finer and more magnificent than in our wildest dreams of the old days we could ever contemplate or imagine.

A library epitomizes in a large sense the labor, experience and wisdom of those who have gone before, and as such becomes a priceless treasure for those who follow. This great store of technical letters has been built up and accumulated by gift, purchase, and exchange through many long years of effort and devotion, often at considerable sacrifice in time and money by those having it in charge. It is therefore a matter of intense satisfaction to the few of us, and particularly the present librarian, Alfred Rigling, who have been identified with its past struggle for existence and development to see this splendid collection of technical and engineering literature safely, beautifully, housed and equipped for its continued care, usefulness and development.

Of all the valued possessions of this great Institute I place its library first and foremost. It is no disparagement to other attributes to believe it will endure in usefulness and value when interest in other departments wanes as times and customs change. We must therefore cherish this library as a priceless gift to posterity, a heritage of accumulated knowledge and experience recording in particular the development and expansion of our American economic and industrial civilization, a matter upon which we are beginning to have a few qualms and some misgiving.

DR. TAGGART:

You can now understand why I refrained from saying anything about the Library in the presence of our next speaker who has handled all of the 110,000 volumes on our shelves.

One year ago our Librarian completed fifty years of faithful service with The Franklin Institute, but on account of illness was unable to be present to celebrate that event with us. We are happy to have him with us tonight and congratulate him now on having completed fifty-one years of service, and express the hope that he may be spared to us for many years to come.

In addition to his duties as Librarian, he has, for a number of years, served as Assistant Editor of the JOURNAL OF THE FRANKLIN INSTITUTE.

Ladies and gentlemen—Mr. Alfred Rigling.

MR. RIGLING:

Mr. Chairman: I have waited nearly fifty years for these ceremonies. About 1885 I witnessed the first attempt to acquire a new building. A few years later another attempt was made and at that time the *Philadelphia Press*, one of the leading newspapers, published a story of the proposed building. It had across two columns at the top of the first page a picture of a beautiful stone building with the caption "Palace Home for Science." This undertaking also proved to be a mirage.

Not many years after this the management announced another plan. This time the building was to be at Fifteenth and Chestnut Streets. It was to contain accommodations for all the departments of the Institute, with lecture halls, committee rooms, library, class rooms, etc. The upper floors were to be leased to engineers, chemists and other professional men. The site was the property of the Hon. John Wanamaker and he offered it to the Institute for $750,000. In all these early attempts at acquiring a new building there was always one unimportant, one trifling detail which stood in the way—money!

However in 1908 things began to look more rosy. Two good friends of the Institute, Mr. Alfred C. Harrison and Mr. John T. Morris, purchased four dwellings for the Institute at Sixteenth and Arch Streets. This was the beginning of a real attempt at a new home. Then the City Fathers and a few artistically inclined persons decided that the Southeastern end of the Parkway should be shifted slightly in a Southwesterly direction in order that the City Hall tower might be in the center of the picture when looking down the Parkway. After the Parkway had been sufficiently wiggled the four properties purchased for the Institute were in the middle of the street and the building project was halted for a time. What happened five years later most of you recall. A site was obtained at Nineteenth and Race Streets.

And finally the new building has become an accomplished fact. It is larger, more imposing and more suited to the activities of the Institute than anything the founders or their immediate successors dared vision in their dreams.

The books have been transferred from the old building and we of the library are now prepared to serve our readers.

When the staff has completed certain tasks I hope we shall be able to substantiate the claim that this is the most useful technical library in the East—if not in the United States.

The meeting then adjourned to Pepper Hall, the reading room of the Library of The Franklin Institute. This hall was named in honor of the Honorable George Wharton Pepper, former Senator of the State of Pennsylvania, in recognition of the service which he rendered in connection with the campaign for funds which was conducted by the Benjamin Franklin Memorial, Incorporated, and The Franklin Institute in 1930. The dedicatory remarks were made by Dr. Howard McClenahan, Director of The Franklin Institute. He spoke as follows:

Ladies and Gentlemen, Friends and Members of The Franklin Institute: This meeting tonight, as Mr. Rigling has stated, represents the consummation of an effort of fifty years, not only an effort which extends over fifty years on the part of The Franklin Institute, but a much more recent effort by the Benjamin Franklin Memorial, Inc.—an effort to pay proper honor to Franklin in the city of his adoption, the city of his fame, the city to which he contributed so many things.

Tonight we rejoice that we can call an accomplished fact the project which was launched in December 1929, resulting in the campaign for funds in June 1930, and now today in the occupation of this building which has been erected as the world's greatest memorial to Benjamin Franklin.

Many of you present participated in the campaign in 1930. I am certain that those who did participate got more fun from it than they ever did from any other project in which they shared. You will remember the luncheons which we held, you will remember the joy caused by the more and more successful reports which were made there, you will recall the lesson that we were teaching to the City of Philadelphia that

it, the City, which thought it could not do a big thing handsomely, could do it, and did it in an exceedingly handsome manner. You will remember the two outstanding figures at these luncheons: One of the most amazing and outstanding was Mr. Cyrus H. K. Curtis, whose courage and leadership and generosity made this building a possibility. We shall later unveil a tablet to him.

There was one other figure in that campaign, the man who gave us spiritual leadership; we certainly could not have built the building but for Mr. Curtis, but I think we could not have had success in our campaign without George Wharton Pepper. You will all recall the charming personality of the man, the humor of the man, and you will remember what a treat it was to have him preside over these meetings. You will not understand, unless you were intimately associated with him, the guidance, the wisdom, the peacemaking. He is not ordinarily thought of in that respect but he kept the peace among all of us who were excited and nervous.

At one of these luncheons it was my privilege to announce that the Board of Managers of The Franklin Institute had voted that two of the rooms in this building should be named in honor of these two gentlemen, one Curtis Hall and the other Pepper Hall, the reading room of the library which should be known by that name as a token of appreciation of the great help and the splendid leadership which was given to us by the Honorable George Wharton Pepper.

(Turning to Mr. Pepper) I would like to say to you, sir, that none of us who were privileged to work under you at that time can fail to remember the joys of those twelve days during the course of which, when the bottom of the stock market was going to the bottomless pit, we took in five million dollars, the amount of money which made it possible for the Benjamin Franklin Memorial, Inc., and The Franklin Institute to build this building. As a token of that feat and a token of our admiration for you, it is our privilege to name this hall Pepper Hall.

We shall place here at this end of the room the legend "Pepper Hall." We shall place here a tablet. I had a tablet and Mr. Pepper would not have it; so we have had a

humbler tablet made which shall be put in, which is expressive of our devoted appreciation of all that he did for us.

And so, ladies and gentlemen, from this time on this hall, the reading room of the library of The Franklin Institute, made possible through the generous efforts of the Benjamin Franklin Memorial Inc., sponsored by The Poor Richard Club, and The Franklin Institute, shall be known as "Pepper Hall."

We appreciate your friendliness in coming here tonight. We ask you to look around, go into the stacks, and make yourselves at home.

STATED MONTHLY MEETING, APRIL 18, 1934.

The regular monthly meeting of the Institute was called to order by the President, Mr. Nathan Hayward. He called upon the Secretary for the business of the meeting.

The Secretary reported that the full minutes of the March meeting had been printed in the JOURNAL of the Institute for April and moved that the minutes be approved as printed. Upon motion this action was taken.

The Secretary reported that it was customary for the Institute to elect to Honorary Membership the recipients of the Franklin Medals in each year. He, therefore, moved upon the recommendation of the Board of Managers that Professor Henry Norris Russell of Princeton University and Dr. Irving Langmuir of the General Electric Company of Schenectady be elected to Honorary Membership. This motion was adopted unanimously.

There being no further business, the President presented as the speaker of the evening Dr. W. F. G. Swann, Director of the Bartol Research Foundation of The Franklin Institute. Dr. Swann spoke delightfully and illustrated his talk with many very striking experiments. His talk was followed by many interesting questions from members of the audience.

The meeting adjourned at ten-five P.M.

HOWARD MCCLENAHAN,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, April 11, 1934.)

HALL OF THE INSTITUTE,
PHILADELPHIA, APRIL 11, 1934.

MR. CHARLES D. GALLOWAY *in the Chair.*

The following reports were presented for final action:

No. 2971: Centrifuge-Microscope.

This report recommended the award of John Price Wetherill Medals to Professor E. Newton Harvey, of Princeton, New Jersey, and Mr. Alfred L. Loomis, of Tuxedo Park, New York, "In consideration of the ingenuity and novelty of the Centrifuge-Microscope through which science is given a new tool of value and much promise."

No. 2980: Work of Mr. Ernst Georg Fischer.

This report recommended the award of the Howard N. Potts Medal to Mr. Ernst Georg Fischer, of Washington, D. C., "In recognition of a lifetime spent with marked success in the design of precise instruments."

GEO. A. HOADLEY,
Secretary to Committee.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, April 18, 1934.)

RESIDENT.

DR. WILLIAM MCAFEE BRUCE, Research Chemist, The Permutit Company, New York City. For Mailing: 312 Broad Street, Mt. Holly, N. J.

DR. LEWIS W. BUTZ, Director of Laboratory Division, Dr. D. Jayne and Son, Inc. For Mailing: 4301 Spruce Street, Philadelphia, Pa.

MR. E. R. FENIMORE JOHNSON, President, Mechanical Improvements Corporation, Camden, New Jersey. For Mailing: Bridgeboro Road, Moorestown, N. J.

MR. FRANKLIN C. OERTLE, Clerk, c/o Charles H. Oertle, Philadelphia, Pa. For Mailing: 521 Levick Street, Lawndale, Pa.

MR. ANDREW MIEDWIG, Civil Engineer in Building Engineering Division, United Engineers and Constructors, Inc., Philadelphia, Pa. For Mailing: 1301 Edgewood Road, Brookline, Upper Darby, Pa.

MR. LOUIS S. POTSDAMER, Consulting Chemical Engineer, Industrial By-Products and Research Corporation. For Mailing: 2201 Chestnut Street, Philadelphia, Pa.

MR. WALTER SCHULZ, Research Chemist, Dr. D. Jayne and Son, Inc. For Mailing: 1421 Arch Street, Philadelphia, Pa.

DR. HELLMUTH C. SCHWALBE, Technical Director, Dill and Collins, Inc. For Mailing: 6323 Magnolia Avenue, Philadelphia, Pa.

MR. CURTIS C. WALLACE, Research Engineer, Electric Storage Battery Company. For Mailing: 7223 Emlen Street, Philadelphia, Pa.
MR. CHARLES WASSERMAN, Manufacturer, Philadelphia, Pa.
DR. ALFRED WOLF, Physicist, Philadelphia, Pa. For Mailing: 5 Surrey Road, Melrose Park, Pa.

STUDENT.

MR. JOSEPH ASHBROOK, Philadelphia, Pa.
MR. ALAN W. BERNHEIMER, Philadelphia, Pa.
MR. WALTER BILLMAN, Instrument Maker, Philadelphia, Pa.
MR. LEYORK CHEESEMAN, Salesman, Philadelphia, Pa.
MR. MOSHA CORNFELD, Philadelphia, Pa.
MR. WALTER M. DOTY, Philadelphia, Pa.
MR. PAUL EGLICK, Philadelphia, Pa.
MR. H. NAT. SCHESTACK, Philadelphia, Pa.
MR. JACK SCHUTZBANK, Philadelphia, Pa.
MR. J. GORDON SMITH, Philadelphia, Pa.
MR. ALEXANDER J. YENULIS, Philadelphia, Pa.

MUSEUM MEMBERSHIP, FAMILY.

MR. ALGERNON R. CLAPP, Pembroke and Fishers Roads, Bryn Mawr, Pa.
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Mr. and Mrs. Stanley G. Flagg, Philadelphia, Pa.
Major W. J. Hammer, New York City.
Mr. James Lyman, Evanston, Illinois.
Major General George O. Squier, Washington, D. C.

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BOOK REVIEWS.

THE PRINCIPLES OF METALLURGY, by Donald M. Liddell, and Gilbert E. Doan, Ch.E., Ph.D., 626 pages, illustrations, 15 × 23.5 cms. New York and London, McGraw-Hill Book Co., Inc., 1933. Price $5.50.

A book such as "The Principles of Metallurgy" will always be welcomed by every individual having a direct or indirect interest in the winning of metals from their ores and their fabrication in both the pure and alloyed state. The character of the book would lead one to classify it as a "happy medium." As such, it will furnish a general view of the subject to the engineering student not adopting metallurgy as a life work, yet at the same time provide a proper foundation for the student who intends to become a metallurgist.

It was not meant that the book should contain masses of detail such as is sometimes found in publications on this subject. Rather the authors have stressed those principles which rate high in importance and although more general in nature, there has been no sacrifice of accuracy. This being the case, it well may serve in the capacity of a quick reference to basic data, something which should constantly prove of value to metallurgical and mining engineers.

The subject matter covers considerable latitude and includes practically every phase of metallurgical operation and development. An Introduction briefly sketching the emergence from antiquity of the art of extracting metals from their ores, is followed by a chapter on "Economic Considerations in Metallurgical Processes." A chapter more timely than ever before.

The main body of material is divided into three sections. The first deals with "Materials Consumed in Metallurgy." These include ores, slags and fluxes, refractories and furnace linings, fuels, air and water. The principles involved in choosing the proper type of slag or flux for each particular smelting operation give the reader a much better insight to the rapidly developing scientific basis of metallurgical operations. Probably in no other industry is the choice of refractories so important to the ultimate result.

The second section is concerned with "Extractive Processes and Apparatus" and probably is the most descriptive portion of the book. The principal topics are the three widely used methods of extracting metals from ores: the Pyro-, Hydro-, and Electrometallurgical. Of course, the pyro or fire metallurgical methods are best known and enjoy the precedence of antiquity. However, the other two exhibit a rapid development that apparently has not yet resulted in any conscious recognition of their possible limitations. The topics of briquetting and sampling, dust and fume control, the measurement of temperature, all find a logical sequence in the section.

The last portion of the book deals with the subject of "Physical Metallurgy." Here are discussed the atomic structure of the metals and alloys, the relation of properties to structure, the technology of shaping metal, and testing. The relation between crystalline formation and the physical properties of a metal are well illustrated. A discussion of alloys naturally involves the use of diagrams. Here again the authors have labored to provide typical examples. A final chapter on Slags, Matte, Bullion and Speiss cannot be ignored if the picture is to be complete. A consideration of the melting points, viscosities, heats of formation and the specific gravities of slags cannot be ignored in the scheme of successful pyrometallurgical operations.

Perhaps the authors have best summarized their own work. They write: "It is our conviction that in an industrial world where change is the continuous order of the day, it is more important to develop a way of thinking about metals, a way of understanding their behavior, in short a 'philosophy of metals,' than it ever can be to memorize any information, of temporary interest, about individual metals and alloys."

T. K. CLEVELAND.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS.

Report No. 474—Nomenclature for Aeronautics, by National Advisory Committee for Aeronautics, 37 pages, illustrations, 23 × 29 cms. Washington, Superintendent of Documents, 1933. Price ten cents.

The nomenclature for aeronautics presented in this Report No. 474 is a revision of the last previous report on this subject (Report No. 240), which was issued in 1926.

This nomenclature was prepared by a special conference on aeronautical nomenclature authorized by the executive committee of the National Advisory

Committee for Aeronautics, under the chairmanship of Dr. Joseph S. Ames. The conference was composed of representatives of the Army Air Corps, Bureau of Aeronautics, Navy Department, Bureau of Standards, Aeronautics Branch, Department of Commerce, and the National Advisory Committee for Aeronautics.

This report supersedes all previous publications of the Committee on this subject. The text has been revised and new sketches have been inserted to replace obsolete photographs.

This report is published for the purpose of encouraging greater uniformity and precision in the use of terms relating to aeronautics, both in official documents of the Government and in commercial publications. Terms in general use in other branches of engineering have been included only where they have some special significance in aeronautics, or form an integral part of its terminology.

GAS ANALYSIS BY MEASUREMENT OF THERMAL CONDUCTIVITY, by H. A. Daynes, D.Sc., F.Inst.P., 357 pages, illustrations, 14 × 22 cms. Cambridge, University Press, 1933.

Most of the time-honored methods for analyzing gases and their mixtures were based upon the chemical properties of the constituents. However, the author points out that "There are a number of physical properties which vary considerably from one gas to another and may, therefore, be used as a means of identification or estimation of a particular gas in a given mixture. Hydrogen, for example, is widely different from oxygen in thermal conductivity, density, refractive index, viscosity, and specific heat." In theory, any one of these physical properties might be utilized to distinguish one gas from another but that of measuring the thermal conductivity by the hot-wire method is found to have outstanding advantages in accuracy, simplicity and speed of working.

The author addresses his book to all whose work involves the analysis of gases. Its object is to assist them in deciding whether the thermal conductivity method has any advantage for their purpose over the older-established methods and, if so, what is the best technique to adopt. Possible applications of the hot-wire method are numerous and varied. In many industries this method of gas analysis has been used for many years and its indispensability established beyond a question. On the other hand, the method has been subjected to much careful investigation in a number of laboratories with the result that many additional applications of the hot-wire method have been developed although not yet extensively employed on a practical scale.

Engineers and those technical men responsible for the proper operation of plants will be vitally interested in the valuable assistance offered by these hot-wire instruments. In the matter of combustion control they present a convenient means of measuring the quantities of carbon dioxide, combustible gases or oxygen present in flue-gases. Similarly they distinctly aid in the operation of blast furnaces, cement kilns, ceramic ovens and internal combustion engines by providing a constant and accurate check on the composition of the exhaust gases. In the case of fuel gases such as producer, blast furnace, coke oven, water and town gases, the hot-wire meter may be operated to show readily the carbon-dioxide, monoxide and hydrogen contents. Gases from liquid air: oxygen, nitrogen, argon, helium and neon, all these may have their purities checked by the thermal conductivity method. In that recently matured industry, the

fixation of atmospheric nitrogen, continuous measurements must be conducted on the hydrogen and nitrogen for purity, the hydrogen-nitrogen ratio and the composition after the reaction, as also the percentage of ammonia in air for the synthesis of nitric acid.

The fact that the hot-wire method can be used to detect gas leakage, particularly into the air, renders it especially useful in aeronautics. It not only detects dangerous percentages of hydrogen in the air of sheds and airships but serves to determine the permeability of balloon fabrics and the seams. In addition, many miscellaneous industrial applications may be cited. These include the determination of hydrogen in electrolytic oxygen and storage battery ventilation ducts; methane in air and in coal mine atmospheres; carbon dioxide in fruit storages, in breweries and in the manufacture of soda; sulfur dioxide in sulfur burner gases; vapors of organic solvents in the plants manufacturing artificial silk, photographic film, smokeless powder, rubber-proofed fabrics; also, the dissolved oxygen in boiler-feed waters. In the field of scientific research, the thermal conductivity method may be used for studying the heat flow through gases, the diffusion of gases through membranes or by thermal activation, the course of gas reactions, the performance of internal combustion engines and the measurement of gas flow. In physiological laboratories the meters can be used for the analysis of alveolar air. An autographic record of the carbon dioxide from a house fly is shown—the meter was the ghost-writer. In botanical work, the respiration and assimilation of carbon dioxide is studied in a similar manner.

The author is to be commended for the very complete treatment of his subject. The first part, Chapters I–XII, deals with the development and scientific basis of the method, the necessary apparatus, and the technique of measurement, without reference to particular applications. This part is intended for those who propose to use the method for new uses or general investigational work. The latter part of the book deals with such practical applications as already mentioned. Undoubtedly this book is the forerunner of many future volumes on the subject of Thermal Conductivity as applied to gas analysis. Dr. H. A. Daynes has set a worthy example.

T. K. CLEVELAND.

CHEMICAL PATENTS INDEX, A COMPREHENSIVE AND DETAILED INDEX OF THE SUBJECT MATTER OF SPECIFICATION AND CLAIMS OF UNITED STATES PATENTS, by Edward Chauncey Worden, 1915–1924, vols. III, IV, V, Subject Index, F to Z. New York, The Chemical Catalog Company, Inc., Price $25.00 per volume.

It always is a pleasure to herald the successful completion of a colossal and arduous task. Only a few years ago this Journal welcomed the publication of Volume One of the Chemical Patents Index series. All those interested in the patented applications of chemical compounds having the first two alphabetical letters as initials, rejoiced that such a labor saver to literature research was now available. They who fostered those chemicals bearing the three initials (C, D, E) next in line, patiently waited another year. However, there were still twenty-one other letters in the alphabet and the chemists chiefly interested in Zirconium and its compounds seemed to be in for a long discouraging wait. Nevertheless, all things must come . . ., and in rapid succession the three final volumes have

now become available to the eager waiters. Volume Three includes the subject index F–L; Volume Four, M–R; and last but not least, Volume Five, S–Z.

The five volumes comprise a total of 5321 pages bearing a total aggregate of about 831,280 separate references for the letters A–Z. All this for the ten years covering 1915–1924 inclusive. Although each single reference has been checked back from galley proof to index card and from page proof to galley, the author feels that mistakes must inadvertently creep in. The author and associates will deem it a courtesy to have attention called to such errors readers may discover.

Only those who at one time or other have been commanded or felt it incumbent upon them, to look up all the patents covering the use of some certain chemical, can fully appreciate the worth of these volumes. Their only regret will be that the author must wait until the end of this year (1934) before he can commence work upon the following decade—if he will.

T. K. CLEVELAND.

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Chemical Patents Index, A Comprehensive and Detailed Index of the Subject Matter of Specification and Claims of United States Patents, by Edward Chauncey Worden, in five volumes, volume 5, Index of subjects S to Z. 1091 pages, 17 × 25 cms. New York, Chemical Catalog Company, 1934. Price $25.00.

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Handbook of Technical Instruction for Wireless Telegraphists, by H. M. Dowsett, fifth edition, 571 pages, illustrations, 14 × 22 cms. London, Iliffe & Sons, Ltd. Price 15 shillings.

Chemical Economics, by Williams Haynes, 310 pages, illustrations, 14.5 × 22.5 cms. New York, D. Van Nostrand Co., 1933. Price $3.25.

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CURRENT TOPICS.

Green Wrappers.—(U. S. D. A. Clip Sheet, No. 815.) After chemists of the Department found that glass or paper containers of a grass green color cut off the light rays which hasten rancidity, a large company marketing fish products has adopted a new green parchment cover which it is hoped will better preserve the flavor of the contents. Although the findings of scientists in public employ are public property, the seafood company is reported to have obtained an agreement from the manufacturers of the parchment paper not to sell the same shade to any competitor.

C.

Baby Food and Dialysis.—Dialysis, a process well-known to the resourceful colloid chemist has been applied to a large-scale method for recovering milk albumin from sweet whey by scientists of the Federal Bureau of Dairy Industry. If a suspension of milk albumin in salt water is placed in a collodion bag and this bag suspended in pure water, the dissolved salts will pass through the collodion membrane finally leaving the albumin in water practically free of any dissolved material. This process is known as dialysis. When the removal of dissolved salts is accelerated by an electric current it is known as electro-dialysis.

The chief value of milk albumin recovered by this new method will be as an ingredient of modified infant foods. Cow's milk, which contains less than half as much albumin as human milk, has a tendency to coagulate in large masses which digest slowly in the infant stomach; whereas human milk coagulates in the stomach in five flocks and is easily digested. The addition of powdered albumin to cow's milk produces a change so that the total albumin is coagulated into a finely divided curd much like that of human milk.

Albumin, as prepared at present, has little value because its solubility is destroyed in the separation process. By this new method, the skim milk is concentrated to the point where the milk sugar may be crystallized out. The liquid may then be dried without impairing the solubility of the albumin, but the salt content of the resultant powder would be so high it could not be used for modifying cow's milk. Therefore, the salts are first removed from the mother liquor by electro-dialysis. After that the albumin is dried to a powder.

C.

Zinc in Relation to Hygiene.—CECIL K. DRINKER AND LAWRENCE T. FAIRHALL (*Public Health Rep.*, 1933, XLVIII, 955–961) consider that an upper permissible limit of 5 parts of zinc per million in drinking water is too low; a limit of 30 parts per million is suggested. In water, zinc salts reveal their presence by an unpleasant, astringent taste before the concentration is sufficient to irritate the stomach. However, foods and beverages should not be stored in zinc-lined or galvanized containers. If the food or beverage has an acid reaction, zinc will be dissolved to form simple compounds which are gastric irritants, and their taste may be concealed by that of the food. In the industries, the condition known as "zinc chill" or "metal fume fever" may be produced not only by inhalation of zinc oxide but also by inhalation of oxides or finely divided powders of other metals, hence is not specific. So-called chronic industrial zinc poisoning is not due to zinc but to other substances which contaminate the zinc.

J. S. H.

Anticipation of Vitamins.—An editorial in the *Am. Jour. Pharmacy* (1934, CVI, 42–43) calls attention to the anticipation of vitamins by JOHN URI LLOYD in a lecture delivered in 1878. Lloyd then stated that certain edible plants, such as lettuce, the bulbs and tops of young onions, and early vegetables, contain substances, then designated supportives, which impart to them antiscorbutic properties, and render them of great value in the diet. This was an anticipation of the antiscorbutic vitamin water-soluble C. Lloyd also stressed the value of foods containing chlorophyl in the diet. Today the relationship of chlorophyl to the metabolism of iron is clearly recognized.

J. S. H.

Influence of Fluorine upon the Teeth and Other Organs.—The relationship of mottled enamel, an endemic dystrophy or defect of the teeth, to a high fluorine content of the drinking water has been recognized for several years.

R. M. BETHKE, C. H. KICK, T. J. HILL, AND S. W. CHASE (*Jour. Dental Research*, 1933, XIII, 473–493) have used rats and swine as experimental animals. Addition of fluorine compounds to their ration affected the teeth of these animals producing a hypoplasia (deficient or arrested development) of both the enamel and the dentine. When chemically equivalent masses of various sources of fluorine were used, this result was most marked with sodium fluoride, and least marked with calcium fluoride, while rock phosphate and phosphatic limestone, which contain fluorine, occupied an interme-

diate position. The size of the skull and its proportions were not influenced in rats. In swine, rock phosphate and sodium fluoride caused thickening of the mandible or lower jaw, and widening of the dental arch.

C. H. BOISSEVAIN AND W. F. DREA (*Jour. Dental Research*, 1933, XIII, 495–500) have traced a relationship between the fluorine content of the drinking water and that of the bones and teeth, using quantitative spectroscopic analysis. Thus, the average per cent. of fluorine in (*a*) the enamel, (*b*) the dentine, and (*c*) the bones was 0.065, 0.112, and 0.7, respectively, in human beings resident in Colorado Springs, Colorado, and 0.00. 0.068, and 0.13, respectively, in persons resident east of the Appalachian Mountains. None of the other organs contained fluorine. In fossil bones, the fluorine content was as high as 3.5 per cent. At Colorado Springs, the fluorine content of the drinking water is relatively high, 2 parts per million.

J. S. H.

Transient Transmutations.—(*Science Service.*) The first chemical proof of the artificial transmutation of the elements has been obtained by M. and Mme. F. Joliot, working at Mme. Curie's famous Institute of Radium in Paris. Mme. Joliot in her scientific work uses her maiden name "Irene Curie" and she is the daughter of Mme. Curie, discoverer of Radium.

These two scientists found that if aluminum, boron and magnesium are bombarded by alpha particles from naturally radioactive polonium, positrons are emitted even after the bombardment is stopped. A positron is a positive electron, just recently discovered and looked upon as one of the ultimate particles of matter.

The theory of the mechanism of the artificial radioactivity is that the helium atom (alpha particle) combines with a boron atom forming a nitrogen atom which is unstable and disintegrates into a stable carbon atom with the emission of a positron. In the case of boron the positron emission lasts about fifteen minutes and probably not over 100,000 atoms have become artificially radioactive under the rain of alpha particles. One hundred thousand atoms may sound like a large number but for boron they would not weigh much over 2.10^{-18} grams, hardly enough for a chemical experiment. Besides, the experimenters must work rapidly if they are to accomplish something before all the activity disappears.

A successful method of chemical examination lay in irradiating a small quantity of boron nitride. Ammonia gas was then produced by heating this activated boron nitride with caustic soda. The ammonia was found to be unusual, indicating that the induced

radioactivity had left the boron compound and gone with the ammonia. This was taken as proof that the radioactivated boron was identical with nitrogen. When magnesium and aluminum are bombarded, the unstable radioactive forms of silicon and phosphorus are produced respectively.

C.

Milk in Bags.—If DR. LOUISE STANLEY, Chief of the Bureau of Home Economics, has anything to say about it, people soon will be able to buy skim milk at three cents a quart or less. The Bureau of Dairy Industry has coöperated in testing bags suitable for holding powdered skim milk. A satisfactory container consisted of an outer bag of bond paper and an inner bag made of two layers of glassine, with paraffin between the layers.

Dr. Stanley points out that the development of an appropriate container will place dry skim milk, a valuable food product, within reach of many homes. Previously, the lack of a suitable small low-cost container has kept the price of such a semi-perishable product too high for a universal retail market. Dry skim milk lacks only the fat contained in whole milk but contains everything else except the water. It provides the calcium and phosphorus which are among the chief needs of children, it is high in protein, and it is rich in vitamin G, which some authorities believe to be the factor that prevents pellagra.

C.

Rosin.—Rosin and other closely associated products which fall under the category of "Naval Stores," received more than their usual share of attention at the Spring Meeting of the American Chemical Society. The exact origin of rosin is not definitely established. As such it is not present in the gum which exudes from the incisions on the trunks of the pine trees. Rather it is a result of the treatment received by this exudation when being deprived of its contents of pine oil and turpentine. But, the real beginnings of "oleoresin," the sap of the southern pines, the source of naval stores, are not yet discovered by the scientific workers. They know that oleoresin exists within the living pine from its earliest seedling stage. In mature normal southern pine wood the relatively large vertical resin passages are found to number from 60 to 400 per square inch of cross section. They connect intimately with the network of horizontal parenchyma rays, numbering, in slash pine for example, over 20,000 per square inch of tangential surface.

The periodic chipping of the pine trees causes the oleoresin to exude freely, whereby it is collected in cups attached to the trees.

When this natural gum is heated, a volatile portion is driven off and is known as turpentine. The nonvolatile residue is called "gum rosin" to distinguish it from wood rosin. This latter brand of rosin is produced generally by the action of steam upon the pine wood itself, in the shape of old stumps, slash and other forms of waste. The wood, reduced to chip form, is subjected to the action of live steam which carries off from the wood the natural terpene oils containing both pine oil and turpentine. The rosin remaining can then be extracted with a solvent such as petroleum naphtha. The processed wood can serve as fuel.

Constitutionally, rosin principally consists of organic acids (about 90 per cent.). These acids are not identical with those originally present in the gum or oleoresin because they were altered through the influence of heat. The non-volatile portion of the oleoresin embraces two main groups, the pimaric and the sapinic acids. The greater part of these acids are converted by heat to the one levoabietic acid, the principal constituent of rosin. Rosin also contains pyroabietic acids, the result of prolonged heat treatment. Organic chemists will be particularly interested to know that both levoabietic acid and dextro-pimaric acid are hydrogenated phenanthrene monocarboxylic acid derivatives. Phenanthrene, the basic element, is obtainable from coal-tar.

The uses for naval stores are being extended constantly. Much of the credit for this development is due to the many chemical transformations that have been wrought upon the elementary products. Rosin, as such, has been *persona nongrata* in the paint industry for many years, having been looked upon as a cheapener. However, rosin partially neutralized by lime, or used in the form of lead, manganese, cobalt and zinc resinates, has been found to confer several desirable properties to paints and varnishes. Rosin combined with glycerine gives "ester gum," a valuable lacquer ingredient. It may also unite with wood and grain alcohols to give products which impart semi-plasticizing effects to lacquers.

The use of rosin for sizing paper is well known. Paper making is still very much of an art and the effects obtained with rosin are many and varied. Plenty of research yet remains to be done in this field. Since rosin is an organic acid of complicated structure, it will combine with alkalies to give derivatives of distinct detergent characteristics. For that reason it has been used as a constituent of soaps.

In the making of synthetic camphor, turpentine serves as the chief source of pure pinene the starting material. Producing camphor from pinene is a long and involved process requiring five distinct steps or organic chemical reaction. It is questionable

whether the synthetic process can be continued in the face of natural Japanese camphor importations at a 1933 price of twenty-two cents per pound plus a duty of only one cent.

C.

The Francqui Prize.—Last month the world in general was informed that the Francqui Foundation of Belgium had awarded the 1934 Prize to Abbé Georges Lemaître, Professor of the Theory of Relativity and the History of Physical and Mathematical Sciences of the University of Louvain. This prize is given annually to a Belgian who has made an important contribution to science in such a way as to increase the international prestige of Belgium.

Like his contemporary, Moseley, Abbé Lemaître saw active service in the war. He served as an adjutant of artillery in the Belgian army and received the Croix de Guerre, Yser Medal, Victory and Commemorative Medals. Fortunately, he was spared to science.

Lemaître's theories on the evolution of the universe have been widely discussed during the past two or three years. In general, they supplement those of Einstein and de Sitter. So far, the Lemaître theory of the primitive atom throws new light on the possible origin of the cosmic ray. Recent scientific tests have brought additional support to this theory but the final proof must depend on the future.

C.

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